PHENOMENA, ATOMS AND MOLECULES

by

IRVING LANGMUIR

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An attempt to interpret phenomena
in terms of mechanisms or atomic
and molecular interactions

by

IRVING LANGMUIR

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INTRODUCTION

When I was asked in the spring of 1946 to give a series of five Hitchcock Lectures at the University of California at Berkeley, I chose for the general subject "Science for the Fun of It." This title was suggested to me by the frequent question, "Having fun today?" asked by Dr. W. R. Whitney during his daily tour thru the industrial research laboratory that he founded in 1900.

The present volume in its eighteen chapters contains a collection of twenty papers, roughly one-tenth of the papers that I have published since 1909, when I joined the research group in Dr. Whitney's Laboratory.

The Bibliography at the end of this book contains a nearly complete list of these papers arranged in eight groups, "A" to "H," according to the principal subject matter treated.

A. General Topics, Scientific Research, Philosophy of Science, Incentives in Science and in Industry, Scientific Education.
B. Structure of Matter, of Molecules, Atoms, Crystals, Proteins, and Ferromagnetic Materials.
C. Conduction, Convection and Radiation of Heat, Diffusion, Evaporation in Vacuum and in Gases, Gas-Filled Incandescent Lamps, etc.
D. The Mechanism of Chemical Reactions at High Temperatures and Low Pressures, Catalysis.
E. High Vacuum Phenomena, Vacuum Pumps, Electron Emission and Space Charge Effects.
F. Electric Discharges in Gases, especially at Low Pressures.
G. Surface Chemistry, Adsorption, Surface Tension, Monomolecular Films, Biological Applications.
H. Meteorology and Related Fields, Aviation, Oceanography, Turbulent Motion of Water and Air, Submarine Detection by use of the Binaural Effect, Precipitation Static, Icing of Aircraft.

In these days in which we hear so much about "planned economy" this list of researches emanating from an industrial laboratory may seem incompatible with the "profit motive" which is supposed to dominate industry. As a matter of fact, these researches were not the result of planning but came from a series of discoveries that could not have been foreseen. The incentive was a deep rooted curiosity regarding the fundamentals of science and the work was carried out for the "fun of it."

The idea of establishing a new type of industrial laboratory originated with A. G. Davis and E. W. Rice of the General Electric Company in 1900. The basic knowledge upon which the electrical industry has been built had been acquired slowly during the 19th Century by the great pioneer scientists who, for the most part, were associated with universities throughout the world. The industries had applied this knowledge to useful ends, but had not attempted to contribute to the basic knowledge. Mr. Rice and Mr. Davis, on the other hand, visualized a laboratory, primarily designed not for the solution of known problems but rather for obtaining new fundamental knowledge in broad fields associated with the work of the company.

Dr. W. R. Whitney was chosen as director of this industrial laboratory although his work at the Massachusetts Institute of Technology had been in physical chemistry.

By 1909 when I joined the laboratory, I found that there was more "academic freedom" than I had ever encountered in any university.

During the first three years I studied chemical reactions that take place when various gases are introduced into evacuated glass bulbs containing heated tungsten filaments, and unexpectedly made the discovery that the molecules of hydrogen gas at the high temperatures that can be obtained with this new material, tungsten, break apart to give hydrogen atoms which have very extraordinary properties. The quest for more knowledge regarding this atomic hydrogen finally led to the invention of the gas filled tungsten lamp. This resulted in an improvement of the efficiency of incandescent lamps and made it possible to construct lamps of much greater size or higher candle power. The history of this early work is given in Chapter Seven in the article entitled "Atomic Hydrogen as an Aid to Industrial Research." The title may be aptly paraphrased "How Curiosity Regarding Atomic Hydrogen Served as an Incentive in Industrial Research."

Just about the time that the development of the gas filled lamp seemed to be possible, I began to be puzzled by the fact that in the older vacuum type of incandescent lamp no large currents flowed across the space between the two ends of the lamp filament. To learn why we did not experience any difficulty on this score I began to spend more of my time on the study of the flow of electrons in high vacuum and in gases. This led to work in fields "E" and "F" listed in the bibliography. The article in Chapter Thirteen entitled "Metastable Atoms and Electrons Produced by Resonance Radiation in Neon" is one of the many papers that resulted from this work.

There were also many practical applications in the field of electronics and radio engineering.

It has been the experience of our laboratory that the search for knowledge in new fields by those who are alert to the possible applications, frequently leads to new discoveries. The word, serendipity, coined two centuries ago by Horace Walpole, well describes this situation. Serendipity may be defined as "the art of profiting from unexpected occurrences." Much of the progress, not only in research laboratories but in the world as a whole, depends on serendipity rather than on careful planning directed toward specific ends. Many of the chapters of this volume afford examples of serendipity.

The study of the chemical reactions taking place in contact with heated tungsten filaments in gases at low pressures led to an interest in the mechanism underlying these chemical reactions. The dissociation of hydrogen molecules into atoms involved a great deal of heat absorption. One of the best ways of studying this was to measure the energy necessary to maintain a tungsten wire at a very high temperature in the presence of hydrogen. This was the basis of the work of "Flames of Atomic Hydrogen" given in Chapter Eight, which received application as a new method of welding metals.

The work on surface chemistry (in field G) started from the study of the reactions on solid surfaces and the catalysis involved in the mechanisms of these reactions (field B). It was soon found that most of these phenomena depended upon the presence of a single layer of atoms. This was a new factor which had not been previously considered in connection with the structure of matter. There are many papers, therefore, that deal with the structure of matter in general (field B) and more particularly with the structure of surfaces. In order to find if these relationships were general, work was started with the surfaces of liquids and this gradually led to the study of surface tension and monomolecular films on water and on other liquids. This science of surface chemistry is gradually leading to biological applications. The field "H" given in the bibliography, which includes meteorology, originated from my early enthusiasm for mountain climbing (1893) and skiing (1903). Work during the first World War on submarine detection aroused my interest in the motion of water, particularly as influenced by the effect of wind acting on the surface. This led to studies of the motion of water in rivers and lakes, which later proved useful in connection with war work on smokes and the icing of aircraft.

It has often been said that during war the energies of scientists are taken away from the fields of pure science and are devoted merely to applications. My own opinion is that both world wars have greatly stimulated even pure science by bringing scientists in contact with much wider fields of activity and by providing to the scientists new devices which are of incalculable value in the progress of science.

The electron tube technique developed during the first world war and extended during the second, and now the methods and materials discovered in connection with increased knowledge of nuclear energy, have speeded up by many-fold the progress in several fields of pure science. Through contact with war problems, scientists have been led to combining sciences which would not normally have been brought together.

For example, the active work in meteorology in which Dr. Vincent J. Schaefer and I are now engaged leads us to the modification of clouds and the control of weather by the production of rain and snow using seeding techniques. This work started from war problems on the production of screening smokes and on the prevention of icing of aircraft when flying through certain types of clouds.

Chapter Seven deals largely with the incentives that may lead to progress in the field of industrial research. Several of the other chapters in this book also deal with the problem of incentives motivating scientific work.

Chapter One deals largely with the philosophy of science, but it leads to a philosophy which should be of great importance for all human affairs. It is pointed out in Chapter One that the whole form and content of classical physics was largely determined by the incentives which led the physicist in his work: "He chose as the subjects of his studies those fields which promised great success" involving the discovery of "natural laws." The common belief that science has shown that all things have their causes is, I believe, a mistaken belief, and it rests largely upon the fact that the scientists had an incentive to discover natural laws. They, therefore, went out and did so. After the turn of the century, it became more fashionable or there was a greater incentive in studying the behavior of single particles and electrons. Then they gradually found that other laws governed these phenomena—the quantum laws and the uncertainty principle.

We, therefore, have to deal with "convergent phenomena" and "divergent phenomena." In human affairs, we have to deal largely with divergent phenomena which are not determined by definite relations of cause and effect.

Much of my work in connection with meteorological phenomena has largely been stimulated by this belief that the essential detailed phenomena of meteorology are not subject to definite relations of cause and effect. They are determined rather by probabilities, and the neglect of such factors has led to entirely false opinion as to the possibility of weather forecasting for the future.

Chapters Two and Three also deal largely with incentives. In both of these, there is some discussion of the incentives that are used by the Russian government in stimulating its scientists. They believe in a system of positive and negative incentives—rewards for a five-year plan fulfilled and severe penalties, including long stays in Siberia, for those who do not fulfill their plans.

In Chapter Three, which was written shortly after I had attended a meeting of the 220th anniversary of the founding of the Academy of Sciences of the U. S. S. R. in Moscow in 1945, I was over-optimistic in hoping that the Russians could cooperate with the rest of the world. I believe that at that meeting it was the intention of the leaders to make a gesture to the world that they intended to so cooperate, and I also think that they sincerely thought that they could. The atomic bomb which was first tested in New Mexico only about two weeks after our party left Russia probably was the turning point in the Russian plan to cooperate with the scientists of the world. Shortly after that, it must have appeared to the Russian government that their own scientists had deliberately chosen to work on such things as the liquefaction of helium and the use of oxygen in blast furnaces rather than study atomic energy. As a result, I believe that the scientists were no longer trusted and were no longer left in charge of their programs. Instead of that, the scientists are now controlled politically, as we see in the case of T. D. Lysenko in the field of biology, with similar control of the arts such as music. This change of attitude on the part of the Russian government towards its scientists will, I believe, force future scientific developments in that country to follow lines which promise foreseeable advantages to the politicians but seriously discourages all work which might lead to fundamental discoveries.

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Chapter One

SCIENCE, COMMON SENSE, AND DECENCY

Up to the beginning of the present century one of the main goals of science was to discover natural laws. This was usually accomplished by making experiments under carefully controlled conditions and observing the results. Most experiments when repeated under identical conditions gave the same results.

The scientist, through his own experiments or from previous knowledge based on the work of others, usually developed some theory or explanation of the results of his experiments. In the beginning this might be a mere guess or hypothesis which he would proceed to test by new types of experiments. If a satisfactory theory is obtained which seems in accord with all the data and with other known facts, the solution or goal of the investigation is considered to have been reached.

A satisfactory theory should make possible the predictions of new relationships or the forecasting of the results of new experiments under different conditions. The usefulness of the theory lies just in its ability to predict the results of future experiments. The extraordinary accomplishments of the great mathematical physicists in applying Newton's Laws to the motions of the heavenly bodies gave scientists of more than a century ago the conviction that all natural phenomena were determined by accurate relations between cause and effect. If the positions, the velocities and the masses of the heavenly bodies were given it was possible to predict with nearly unlimited accuracy the position of the bodies at any future time. The idea of causation, or a necessary relation of cause and effect, has long been embedded in the minds of men. The recognized responsibility of the criminal for his acts, the belief in the value of education and thousands of words in our language all show how implicitly we believe in cause and effect. The teachings of classical science, that is, the science up to 1900, all seem to reinforce this idea of causation for all phenomena.

Philosophers, considering many fields other than science, were divided in their opinions. Many went so far as to believe that everything was absolutely fixed by the initial conditions of the universe and that free will or choice was impossible. Others thought that cause and effect relations were mere illusions.

From the viewpoint of the early classical scientist the proper field for science was unlimited. Given sufficient knowledge, all natural phenomena, even human affairs, could be predicted with certainty. Ampere, for example, stated that if he were given the positions and velocities of all the atoms in the universe it should be possible theoretically to determine the whole future history of the universe. Practically, of course, such predictions would be impossible because we could never hope to get the necessary knowledge nor the time to carry out such elaborate calculations.

A little later scientists developed the kinetic theory of gases according to which the molecules of a gas are moving with high velocity and are continually colliding with one another. They found that the behavior of gases could be understood only by considering the average motions of the individual molecules. The particular motion of a single molecule was of practically no importance. They were thus taught the value of statistical methods, like those which the insurance company now uses to calculate the probable number of its policy-holders that will die within a year.

The theories or explanations which were developed in connection with the natural laws usually involved a description in terms of some kind of a model. In general, instead of thinking of the whole complex world we select only a few elements which we think to be important and concentrate our minds on these. Thus, the chemist developed the atomic theory according to which matter was made up of atoms of as many different kinds as there are chemical elements. These were thought of as small spheres, but no thought was given as to the material of which they were made. When later theories indicated that these atoms were built up of electrons and positive nuclei this made very little difference to the chemist, for he had not needed previously to consider that aspect of the model.

High-school boys to-day are asked to build model airplanes. These must be of such shape that the different types of airplanes can be recognized when the profiles of the models are seen against a white background. It naturally is not particularly important just what kind of material is used in constructing them. Airplane designers build model airplanes to be studied in wind tunnels, but these do not need to be provided with motors.

Most of the models which the scientist uses are purely mental models. Thus, when Maxwell developed the electromagnetic theory by which he explained the properties of light he thought of a medium through which these waves traveled. This was called the ether. It was supposed to have properties like those of elastic solid bodies. The reason for this choice of a model was that at that time the average scientist had been taught in great detail the theory of elasticity of solid bodies. Thus the magnetic and electric fields could be understood in terms of the familiar elastic properties. At the present time relatively few students are well trained in the theories of elasticity. The situation is thus reversed and to-day we explain the properties of elastic solids in terms of the electrical forces acting between their atoms.

Every student of geometry constructs a mental model when he thinks of a triangle. The mathematical lines that bound the triangle are supposed to have no thickness. In other words, they are stripped of any properties except those that we wish particularly to consider.

Most of the laws of physics are stated in mathematical terms, but a mathematical equation itself is a kind of model. We establish or assume some correspondence between things that we measure and the symbols that are used in an equation, and then, after solving the equation so as to obtain a new relation, we see if we can establish a similar correspondence between the new relation and the experimental data obtained from the experiment. If we succeed in this we have demonstrated the power of the mathematical equation to predict events.

The essential characteristic of a model is that it shall resemble in certain desired features the situation that we are considering. On this basis we should recognize that practically any theory has many arbitrary features and has limitations and restrictions imposed by the simplifications that we have made in the development of the theory or the construction of our model.

Beginning with Einstein's relativity theory and Planck's quantum theory a revolution in physical thought has swept through science. Perhaps the most important aspect of this is that the scientist has ceased to believe that words or concepts can have any absolute meaning. He is not often concerned with questions of existence; he does not know what is the meaning of the question, "Does an atom really exist?" The definition of "atom" is only partly given in the dictionary. Its real meaning lies in the sum total of knowledge on this subject among scientists who have specialized in this field. No one has been authorized to make an exact definition. Furthermore, we can not be sure just what we mean even by the word "exist." Such questions are largely metaphysical and in general do not interest the modern scientist. Bridgman has pointed out that all concepts in science have value only in so far as they can be described in terms of operations or specifications. Thus it doesn't mean much to talk about length or time unless we agree upon the methods by which we are to measure length and time.

For many years, up to about 1930, the new physics based on the quantum theory seemed to be fundamentally irreconcilable with the classical physics of the previous century. Through the more recent development of the uncertainty principle, developed by Bohr and Heisenberg, this conflict has now disappeared. According to this principle it is fundamentally impossible to measure accurately both the velocity and the position of any single elementary particle. It would be possible to measure one or the other accurately but not both simultaneously. Thus it becomes impossible to predict with certainty the movement of a single particle. Therefore, Ampere's estimate of the scope of science has lost its basis.

According to the uncertainty principle, which is now thoroughly well established, the most that can be said about the future motion of any single atom or electron is that it has a definite probability of acting in any given way. Probability thus becomes a fundamental factor in every elementary process. By changing the conditions of the environment of a given atom, as, for example, by changing the force acting on it, we can change these probabilities. In many cases the probability can be made so great that a given result will be almost certain. But in many important cases the uncertainty becomes the dominating feature just as it is in the tossing of a coin.

The net result of the modern principles of physics has been to wipe out almost completely the dogma of causation.

How is it, then, that classical physics has led to such definite clean-cut laws? The simplest answer is that the classical physicist naturally chose as the subjects for his studies those fields which promised greatest success. The aim of the scientist in general was to discover natural laws. He therefore carried on his experiments in such a way as to find the natural laws, for that is what he was looking for. He was best able to accomplish this by working with phenomena which depended upon the behavior of enormous numbers of atoms rather than upon individual atoms. In this way the effects produced by individual atoms averaged out and became imperceptible. We have many familiar examples of this effect of averaging—the deaths of individual human beings can not usually be predicted, but the average death rate in any age group is found to come close to expectation.

Since the discovery of the electron and the quantum and methods of detecting or even counting individual atoms, it has been possible for scientists to undertake investigations of the behavior of single atoms. Here they have found unmistakable experimental evidence that these phenomena depend upon the laws of probability and that they are just as unpredictable in detail as the next throw of a coin. If, however, we were dealing with large numbers of such atoms the behavior of the whole group would be definitely determined by the probability of the individual occurrence and therefore would appear to be governed by laws of cause and effect.

Just as there are two types of physics, classical physics and quantum physics, which have for nearly twenty-five years seemed irreconcilable, just so must we recognize two types of natural phenomena. First, those in which the behavior of the system can be determined from the average behavior of its component parts and second, those in which a single discontinuous event (which may depend upon a single quantum change) becomes magnified in its effect so that the behavior of the whole aggregate does depend upon something that started from a small beginning. The first class of phenomena I want to call *convergent phenomena,* because all the fluctuating details of the individual atoms average out giving a result that converges to a definite state. The second class we may call *divergent phenomena,* where from a small beginning increasingly large effects are produced. In general then we may say that classical physics applies satisfactorily to convergent phenomena and that they conform well to the older ideas of cause and effect. The divergent phenomena on the other hand can best be understood on the basis of the quantum theory of modern physics.

Let me give some illustrations of divergent phenomena. The wonderful cloud chamber experiments of C. T. R. Wilson show that a single high-speed electron or an alpha particle from an atom of radium, in passing through a gas, leaves a trail of ions. By having moisture in the gas and by causing the gas to expand just after these ions are produced, drops of water are made to condense on the ions. By a strong illumination it thus becomes possible to see or photograph this track of ions as a white line on a dark background. The time at which an alpha particle will be emitted from a radium atom is inherently unpredictable. It would be totally contrary to the teachings of modern physics to suppose that our inability to predict such an event is merely due to our ignorance of the conditions surrounding the particular atom. The uncertainty principle requires that even if these conditions were absolutely fixed the time of emission and the direction of emission of the alpha particle are subject to the laws of chance and thus for a single particle are unpredictable.

The occurrences in the Wilson cloud chamber following the disintegration of a single radium atom are typical divergent phenomena. The single quantum event led to the production of countless thousands of water droplets and these made the track of the alpha particle visible and led to its reproduction in a photograph. This track may show some unusual feature of particular interest to the scientist; for example, it may have a kink which indicates that the alpha particle collided with the nucleus in one of the molecules of gas. The photograph may therefore be published—may start discussions among scientists that involve thousands of man hours—may delay one of them so that he misses a train on which he might otherwise have suffered a fatal accident. Examples of this kind, any number of which could be given, show that it is possible for single unpredictable quantum events to alter the course of human history.

The formation of crystals on cooling a liquid involves the formation of nuclei or crystallization centers that must originate from discrete, atomic phenomena. The spontaneous formation of these nuclei often depends upon chance.

At a camp at Lake George, in winter, I have often found that a pail of water is unfrozen in the morning after being in a room far below freezing, but it suddenly turns to slush upon being lifted from the floor.

Glycerine is commonly known as a viscous liquid, even at low temperatures. Yet if crystals are once formed they melt only at 64° F. If a minute crystal of this kind is introduced into pure glycerine at temperatures below 64° the entire liquid gradually solidifies.

During a whole winter in Schenectady I left several small bottles of glycerine outdoors and I kept the lower ends of test-tubes containing glycerine in liquid air for days, but in no case did crystals form.

My brother, A. C. Langmuir, visited a glycerine refinery in Canada which had operated for many years without ever having any experience with crystalline glycerine. But suddenly one winter, without exceptionally low temperatures, the pipes carrying the glycerine from one piece of apparatus to another froze up. The whole plant and even the dust on the ground became contaminated with nuclei and although any part of the plant could be temporarily freed from crystals by heating above 64° it was found that whenever the temperature anywhere fell below 64° crystals would begin forming. The whole plant had to be shut down for months until outdoor temperatures rose above 64°.

Here we have an example of an inherently unpredictable divergent phenomenon that profoundly affected human lives.

Every thunderstorm or tornado must start from a small beginning and at least the details of the irregular courses of such storms across the country would be modified by single quantum phenomena that acted during the initial stages. Yet small details such as the place where lightning strikes or damage occurs from a tornado may be important to a human being.

Much more obvious examples of divergent phenomena which affect human life are those involved in the mechanism of heredity and the origin of species. Whether the genes are inherited from the mother or from the father seems to be fundamentally a matter of chance, undoubtedly involving changes in single atoms. It is known definitely that changes in genes or mutations can be produced by x-rays, and it has even been proved that a single quantum is sufficient to bring about such an alteration. The growth of any animal from a single cell is a typical illustration of a divergent phenomenon. The origins of species and all evolutionary processes, involving as they do natural selection acting upon mutations, must depend at almost every stage upon phenomena which originate in single atoms.

An idea that develops in a human brain seems to have all the characteristics of divergent phenomena. All through our lives we are confronted with situations where we must make a choice and this choice may sometimes alter the whole future course of our lives. Occasionally such decisions are made by tossing a coin—an event which seems unpredictable—but there is no reason to doubt that single atomic processes, or small groups of them which follow statistical laws, may often be a determining element.

When certain bacteria are heated until they begin to die it is found that in successive intervals of time the same fraction of the survivors succumb. This seems to prove that the life of these cells depends on a single unstable molecule whose change involves death. It is thus a matter of pure chance as to which particular individuals die within a given period.

The examples that I have given of convergent and of divergent phenomena are purposely chosen as extreme types. Actually there are many intermediate cases that are not clearly one or the other. Or, again, phenomena which start out to be divergent may apparently degenerate into the convergent type. For example, if the photograph of the Wilson cloud track did not prove to be of interest it would soon be forgotten and might have no further ascertainable effects on human lives. Similarly in the evolutionary process a new species that originates as a single divergent phenomenon may not survive and its effect soon seems to die out.

We must recognize, nevertheless, that a divergent phenomenon which once occurs permanently alters details of molecular arrangements in the convergent systems that follow it and thus conditions may be brought about which favor the occurrence of new divergent phenomena. In a world in which divergent or quantum phenomena occur we can thus have no absolute relation of cause and effect.

As the implications of the uncertainty principle, especially as applied to divergent phenomena, are more generally recognized the limitation of the idea of causality should have profound effects on our habits of thought. The science of logic itself is involved in these changes. Two of the fundamental postulates of logic are known as the law of uniformity of nature and the law of the excluded middle. The first of these laws is equivalent to the postulate of causality in nature. The second law is simply the familiar postulate that a given proposition must be either true or false. In the past these so-called laws have formed the basis of much of our reasoning. It seems to me, however, that they play no important part in the progress of modern science. The cause and effect postulate is only applicable to convergent phenomena. The second postulate in assuming that any proposition must be true or false implies that we attach absolute meanings to words or concepts. If concepts have meanings only in terms of the operations used to define them we can see that they are necessarily fuzzy. Take, for example, this statement, "Atoms are indestructible." Is this true or false? The answer depends upon what aspect of atoms is considered. To the chemist the statement is as true as it ever was. But a physicist, studying radioactive changes, recognizes that some atoms undergo spontaneous disintegration or destruction. The fact is that the chemist and the physicist have no exact definitions of the word "atom" and they also do not know in any absolute sense what they mean by "indestructible."

Fortunately such questions no longer occupy much of the time of scientists, who are usually concerned with more concrete problems which they endeavor to treat in common-sense ways.

It is often thought by the layman, and many of those who are working in so-called social sciences, that the field of science should be unlimited, that reason should take the place of intuition, that realism should replace emotions and that morality is of value only so far as it can be justified by analytical reasoning.

Human affairs are characterized by a complexity of a far higher order than that encountered ordinarily in the field of science.

To avoid alternating periods of depression and prosperity economists propose to change our laws. They reason that such a change would eliminate the cause of the depressions. They endeavor to develop a science of economics by which sound solutions to such problems can be reached.

I believe the field of application of science in such problems is extremely limited. A scientist has to define his problem and usually has to bring about simplified conditions for his experiments which exclude undesired factors. So the economist has to invent an "economic man" who always does the thing expected of him. No two economists would agree exactly upon the characteristics of this hypothetical man and any conclusions drawn as to his behavior are of doubtful application to actual cases involving human beings. There is no logical scientific method for determining just how one can formulate such a problem or what factors one must exclude. It really comes down to a matter of common sense or good judgment. All too often wishful thinking determines the formulation of the problem. Thus, even if scientifically logical processes are applied to the problem, the results may have no greater validity than that of the good or bad judgment involved in the original assumptions.

Some of the difficulties involved in a scientific approach to economic problems is illustrated by the following: If we wish to analyze the cause of a depression (or for example, a war) we should ask ourselves what we mean by the word "cause" in this connection. In terms of operations the usual meaning of the word cause is something as follows: It is a common experience, in a study of convergent phenomena, that if a given set of physical conditions are brought about repeatedly at different times, the same result occurs in each case. Except in so far as it is possible to repeat the experiment and get the same result it is impossible to give a definite meaning to the word cause.

In the case of a depression or a war, we logically need to produce, or at least to observe, a given set of possible antecedent conditions and to see whether they are always followed by depressions. Since we can not produce experimental depressions, nor have we sufficient observational data to enable us by statistical means to unravel the enormous number of factors involved, we must conclude that the word "cause" as applied to a depression has an extremely fuzzy meaning.

When we consider the nature of human affairs it is to me obvious that divergent phenomena frequently play a role of vital importance. It is true that some of our historians cynically taught most of our college students from 1925 to 1938 that wars, the rise and fall of a nation, etc., were determined by nearly cosmic causes. They tried to show that economic pressure, and power politics on the part of England or France, etc., would have brought the same result whether or not Kaiser Wilhelm or Hitler or any other individual or group of individuals had or had not acted the way they did. Germany, facing the world in a realistic way, was proved, almost scientifically, to be justified in using ruthless methods—because of the energy and other characteristics of the German people they would necessarily acquire and should acquire a place in the sun greater than that of England, which was already inevitably on the downward path.

I can see no justification whatever for such teaching that science proves that general causes (convergent phenomena) dominate in human affairs over the results of individual action (divergent phenomena). It is true that it is not possible to prove one way or the other that human affairs are determined primarily by convergent phenomena. The very existence of divergent phenomena almost precludes the possibility of such proof.

The mistaken over-emphasis on convergent phenomena in human affairs and the reliance on so-called scientific methods have been responsible in large degree for much of the cynicism of the last few decades.

The philosophy which seems to have made the German people such willing aggressors is allegedly based upon scientific realism. Almost any system of morality or immorality could receive support from the writings of Nietzsche, so inconsistent are they with one another. But his teachings, which purport to be based on the laws of natural selection, have led in Germany to a glorification of brute strength, with the elimination of sympathy, love, toleration and all existing altruistic emotions.

Darwin, himself, however, recognized that the higher social, moral and spiritual developments of mankind were factors which aided in survival. This is often referred to loosely as the law of the survival of the fittest. The concept of fitness seems, however, inherently rather fuzzy. Apparently those individuals are fittest which possess characteristics that increase the probability that they shall survive.

We often hear realists deplore the effects of charity which tend to keep the unfit alive. We are even told that the whole course of evolution may be reversed in this way. Similar arguments could be used against the surgeon who removes an appendix or a doctor who uses a sulfa drug to cure pneumonia.

But what is the need of developing a race immune to appendicitis or pneumonia if we possess means for preventing their ill effects. The characteristics that determine fitness merely change from those of immunity to those which determine whether a race is able to provide good medical treatment.

The coming victory of the United Nations will prove that survival of a nation may be prevented by an aggressive spirit, by a desire to conquer or enslave the world, or by intolerance, ruthlessness and cruelty. In fact, there is no scientific reason why decency and morality may not prove to be vastly more important factors in survival than brute strength.

In spite of the fact that we can no longer justify a belief in absolute causation and must recognize the great importance of divergent phenomena in human life we still have to deal with causes and effects. After all we must plan for the future. We can do this, however, by estimating probabilities even where we do not believe that definite results will inevitably follow. When our army lands in North Africa its probable success depends on the carefulness of the preparations and the quality of the strategy. But no amount of foresight can render success absolutely certain.

It does not seem to me that we need be discouraged if science is not capable of solving all problems even in the distant future. I see no objections to recognizing that the field of science is limited.

In the complicated situations of life we have to solve numerous problems and make many decisions. It is absurd to think that reason should be our guide in all cases. Reason is too slow and too difficult. We do not have the necessary data or we can not simplify our problem sufficiently to apply the methods of reasoning. What then must we do? Why not do what the human race always has done—use the abilities we have—use common sense, judgment and experience. We under-rate the importance of intuition.

In almost every scientific problem which I have succeeded in solving, even after those that have taken days or months of work, the final solution has come to my mind in a fraction of a second by a process which is not consciously one of reasoning. Such intuitive ideas are often wrong. The good must be weeded out from the bad—sometimes by common sense or judgment—other times by reasoning. The power of the human mind is far more remarkable than one ordinarily thinks. We can often size up a situation, or judge the character of a man by the expression of his face or by his acts in a way that would be quite impossible to describe in words.

People differ greatly in their ability to reach correct conclusions by such methods. Our numerous superstitions and the present popularity of astrology prove how often our minds make blunders. Since we have to live with our minds, we should train them, develop them, censor them—but let us not restrict them by trying to regulate our lives solely by science or by reason.

Our morality is a kind of summation of the wisdom and experience of our race. It comes to us largely by tradition or religion. Some people justify evil things on the basis of morality—but by and large a recognition of right and wrong, even if these concepts are sometimes fuzzy, has proved to be of value to mankind. The philosophical, metaphysical or even scientific analysis of the principles of ethics has not proved particularly fruitful. A sense of morality and decency, even if not scientific, may help win the war.

Chapter Two

DISCUSSION OF SCIENCE LEGISLATION

In my discussion of the legislative proposals for the promotion of science I wish to dwell upon some basic facts and principles which should guide us in formulating this legislation.

The prominent role that the U. S. has played in the second World War has been possible because of certain important characteristics of the American people. I am concerned particularly with those that relate to the progress in science and industry which has been so vital to our war contribution.

Dr. Vannevar Bush in his report, "Science, the Endless Frontier," has stressed the necessity of progress in science, and has shown that basic or fundamental scientific work in the universities of the world has been the foundation on which this progress has been built. I do not want to repeat what he has said so ably.

Since he presented this report we have had the announcement of the atomic bomb and the Smyth report which tells of the scientific and industrial work which led to it. The atomic bomb puts upon the proposed scientific legislation an emphasis and an urgency of a new degree. I have recently attended a four-day conference at the University of Chicago on the subject of the atomic bomb. It was the overwhelming opinion that it will be only a matter of three to five years before other nations, having the requisite industrial power, will be able to construct such a bomb. There is no possibility of permanently keeping "the secret" of the atomic bomb. We thus have clearly a lead of only a few years. The important question is whether we can retain such a lead. For the future security of the world it is, therefore, vitally necessary to strengthen the United Nations organization and ultimately, through a world government, to control atomic energy for the benefit of all mankind rather than have it as a perpetual threat. In any case long range security will depend upon *progress,* particularly, scientific and industrial progress and of course, upon the strengthening of ties between nations making for goodwill and understanding.

I shall endeavor to analyze a little more closely than was done in the Bush report the factors upon which progress in the U. S. has reached the present level. However, before that I would like to consider for a moment the atomic bomb work covered by the Smyth report, in so far as it bears on the question of the planning of scientiific work.

The atomic bomb rests on a foundation of pure science carried on almost entirely in universities in many different nations over a period of years. Without this foundation all the resources of American industry, the organizing power of the Army, and the finances of the Government would never have led to the atomic bomb. The unhampered, free search for truth which was permitted in universities provided the favorable conditions under which such fundamental research progressed. Without such a foundation no planning board could have brought the atomic bomb into existence. It is, of course, equally true that the pure scientists themselves never could have produced the atomic bomb since this required the vast financial resources of the Government, the efficient organization of the Army, the OSRD, and the tremendous industrial power which exists in this country. It is important to note that in the Manhattan Project nearly all of the 2 billion dollars was spent not for fundamental science but for its applications. The final result was obtained only by a remarkably fine example of teamwork or cooperation between scientists, engineers, technicians, Army, and the few high government officials of extraordinarily clear vision and leadership who knew of this project.

It has been pointed out in the Bush report and elsewhere that up to about 1910 the U. S. had already shown remarkable proficiency in developing industries upon the basis of the pure science that had been developed in other countries, particularly Germany, England, and France. However, since about that time the Americans have been contributing much more than before in the field of pure science. Within the last 10 years before the war America was making at least its fair share of the contributions to fundamental science. The larger part of this progress in basic science was done in universities and research institutes but there was an increasing tendency for industrial research laboratories to engage in fundamental research. During the post-war period this tendency will probably develop considerably further.

The remarkable expansion of American industry, which was based upon the applications in science, is well illustrated by considering the following list of industries in which the U. S. took a leading part:

Railroads
Oil
Steel
Aluminum
Electrical, Automobile, and Aviation
Telephone, Radio, Rubber, and many others

There are, of course, many factors which have made America such a great industrial country. I think that the progress resulted primarily from the many types of *incentives* which were active in this country. First of all, by our Constitution an unusually fine patent system was established. A patent is essentially a contract between the Government and an inventor by which the inventor renounces all advantages of secrecy and publishes a full description of the invention *in exchange* for a limited 17-year monopoly. I believe that this patent system more than any other single factor has been responsible for the great industrial progress in our time. The benefits that have accrued to inventors through the use of their patents have been almost negligible compared to the benefits the public has received through the rapid development and use of the inventions stimulated by the wholesome profit motive, which was given by the patents. Some defects in the patent system have developed and should be cured but it would be disastrous in my opinion to weaken the patent system. Even compulsory licensing removes much of the incentive to the inventor and to those who are able to develop inventions. Without adequate patent protection industry would be forced to attempt to keep inventions secret. This would greatly retard our industrial progress.

Another important factor that has stimulated progress is that America had the pioneering spirit. We believed in men. We pushed forward into the unknown. There was keen competition among such leaders and the rewards were great. There thus grew up a system of *free enterprise.* I think that any careful analysis would prove that even the great fortunes amassed by Carnegie, the Vanderbilts, the Rockefellers, etc., were a cheap price to pay for the tremendous advances made by our steel, railroad, and oil industries. I do not mean for a moment to argue that we should again encourage all the abuses that occurred during the early stages of the development of these industries, but I believe the abuses should have been corrected without destroying the major part of the system of incentives that had proved so valuable.

Perhaps, through the sense of fairplay that was characteristic of our love of sports, there developed in America a remarkable spirit of teamwork and cooperation which has been a vital factor in our progress.

The system of free enterprise is part of the capitalist system. The greatest merit of the capitalist system I believe is the very great incentive given to individuals to forge ahead in new fields. We have learned in recent years that the capitalist system has serious defects. The greatest, I think, is its tendency toward instability. Thus, when a depression starts and people lose confidence they stop buying anything more than the necessities of life and thus more people are thrown out of employment. This aggravates still further the causes that led to the depression. In the early days of the U. S. it took the labor of nearly all the people to maintain the people at a relatively low standard of living. Our agricultural and industrial resources have now grown to such a degree that only a very small proportion of the people, smaller than ever before, can produce the necessities of life for the whole population. In a depression it is thus possible to have a greater fraction of unemployment than in the early days. It is, therefore, necessary to modify or control the capitalist system in such a way as to give it more stability and above all, to prevent the threat of widespread unemployment. If we are to have continued progress and keep our lead over other nations, especially in such things as the atomic bomb, it is essential that our modifications of the system should not stifle incentives or initiative.

A guiding principle which the Government could well adopt in establishing control over our capitalist system, including industry, labor, agriculture, etc., would be that the control is needed primarily in those cases where there is a conflict between private interest and public interest. In general, the profit motive on the part of individuals and industries has been in the public interest and has led to progress. Government control is needed particularly where the profit motive is distinctly contrary to public interest.

We have inherited from our past (personal liberty, freedom of thought, free enterprise, patents, etc.) a system of incentives more effective than that existing in any other nation, but the obvious necessity of government control of some features of our capitalist system has frequently led to attacks of the capitalist system *as a whole*: attacks on its good as well as its bad features. Let me give a list of some of the things which are now tending to restrict or even suppress incentives. In giving this list I do not at present wish to favor or oppose any of them. I want merely to call attention to the effects they are having upon incentives.

Anti-Trust Laws. The tendency has been to regard all monopolies as evil, forgetting that in certain cases (telephone, railroads, etc.) monopolies are necessary and beneficial when properly controlled.

Taxation. Individual income taxes, and especially the high surtax rates, have been based on the so-called democratic principle that taxes should be paid *in accord with the ability to pay.* If this principle were carried to its logical conclusion all incomes above an average of perhaps $5,000 per year would automatically go to the government nearly destroying incentives. A much more reasonable principle for taxation would be that taxes would be *distributed according to the best public interest.* With such a principle the importance of retaining incentives would be recognized. The 95 percent excess profits tax for corporations almost wholly destroys the incentive to start new enterprises or to increase the efficiency of old ones.

Although such a measure may have had some justification during war time, it is now pretty generally recognized that it would be very harmful to the public interest to continue it in peace time.

Civil Service Laws. Although the public interest is well served by the application of the Civil Service laws to perhaps 90 percent of the government employees now acting under them, such laws produce an almost disastrous effect on certain kinds of government projects which require men of the highly specialized training which is needed among the leaders in government scientific research laboratories. Some important Army and Navy post-war research projects must be assigned to private industrial laboratories almost solely because of the known impossibility of carrying on this work in Government laboratories under Civil Service restrictions.

Veteran Preference. It is usually fair and in the public interest to give veterans preference over others when giving employment. It must be recognized, however, that this is a type of class legislation which, in other cases, is thought to be undesirable. In the research institutes, which we are now considering in these science bills, the granting of a preference to veterans may frequently lead to serious loss of efficiency and so prevent a research organization from attaining its objectives. There should be special provisions for excluding key men engaged in work of this kind from the provisions of laws that put veterans in a special class. The criterion should be whether such action is in the public interest.

Social Security Laws. Old age pensions, unemployment compensation, the "right to a job" often tend to remove incentives which would be in the public interest.

Moratoriums on Mortgages, etc.

Labor Unions frequently take a strong stand against *piece work rates.* In some cases they have insisted that both skilled and unskilled workers receive the same pay even when it means a reduction of pay of the more skilled workers. Such practices, I believe, are decidedly not in the public interest for they lead to inefficiency and the loss of incentives and freedom of opportunity to individual workers.

Attacks on the Patent System. These attacks, if successful, would destroy, as I have said before, the greatest single incentive which has underlaid the great industrial progress in America.

The many attempts at regimentation of labor, industry, agriculture, etc., are against public interest largely because they would remove incentives. War time secrecy regulations, if carried over into peace time, would have a similar effect. When scientists are not able to publish the results of their researches, their opportunities and recognition are so reduced that laboratories under such regulations will find it difficult to maintain a high class of scientific personnel.

From the foregoing discussion it will be recognized that in the U. S. we have a *dual system* of incentives. From the capitalist system we have inherited an extremely effective set of incentives. It is generally recognized that the large spread in pay between different jobs of various types is quite proper and has played an important part in the development of our industries and in our general standard of living. Nobody reasonably expects that the president of a large corporation should receive the same pay as his least paid employee. On the other hand, we have been taking it for granted that the government should recognize no class distinctions but should treat all its citizens as equals. Occasionally this is qualified by saying all should have equal opportunities. It cannot be maintained that men are equal in abilities, in skills, or in usefulness to the community. If all men are to be made equal in fact, the question arises whether it is worthwhile to have equal opportunities merely to become equal to everyone else. Progress depends upon the opportunity of exceptional men to become leaders.

During the war, especially since 1943, scientific war work for the Army and Navy has frequently been greatly retarded by the failure to defer young men of exceptional training or ability. No other country suffered as greatly as we did from this short-sighted policy. This has been emphasized in the Bush report. Since the end of the war, the reasons for drafting men, especially those needed for reconversion of our industries to a peace time basis have now largely disappeared. Yet we find that our reserves of scientific men are now being depleted faster than ever before because their work in industries or government laboratories is no longer a valid reason for deferment. This subject has been very ably discussed by Walter J. Murphy in an editorial in the September number of *Chemical and Engineering News*. Those who have read what the Bush report has to say on the unwise drafting of scientific men should also read this article by Murphy to bring his information up to date.

Incentives in Russia. I was invited to attend the 220th anniversary of the founding of the Academy of Sciences of the USSR in Leningrad and Moscow last June. I was particularly impressed by the tremendous emphasis placed upon incentives in Russia today. Since 1931 the Soviet Government has adopted the policy that the rates of pay should be determined not by a man's needs but by his services to the state. They seem to have carried this policy through consistently and successfully. It is continually being pointed out by the Russians that their system of incentives brings efficiency and is thus one of the main factors that will help to make Russia great and will make possible a higher standard of living.

They not only pay the industrial workers by piece work rates but they have especially high piece work rates for that part of a man's production by which he exceeds his quota. The pay of the workers is represented only in a small part by the *money* they receive. The main part of the compensation consists of permission to buy rationed goods at low pre-war prices. Surplus money can be used only in markets or stores selling unrationed goods at prices that range from 20 to 100 times pre-war prices. Nearly everything that is essential is rationed (food, clothing, housing, cigarettes, etc.). Thus, their policy of paying a man according to his services to the state takes the form of giving greatly different amounts of rationed goods to men in different positions or having different skills. This seems to be thought of in Russia as a legitimate and desirable practice. Imagine, however, in this country what the public reaction would be if a bill were introduced into the Senate during war time giving six more times red ration points to the president of a company than to one of his lower paid employees. We must remember, however, that in Russia if there are to be incentives, they must come from the government. The government has deliberately chosen to adopt an incentive system which is at least as effective and as logical as that which we have inherited from our capitalist system before it was restrained by government control.

Among the directors of the scientific institutes in the Russian Academy of Sciences I found striking evidence of this incentive system. Automobiles with chauffeurs, who could be called upon at 3 A.M., were supplied at government expense to such men. One director told me that although he already has a summer home provided for him, the government has recently offered to build him another summer home in the mountains.

The incentives offered to scientists in Russia do not consist wholly of their compensation in money or in ration points. Just before the anniversary meeting of the Academy, 13 Russian scientists were awarded the much coveted order "Hero of Socialist Labor," the highest honor bestowed by the Soviet Government to a civilian. A total of 1400 orders of lesser degree were also distributed. In this and other ways the social prestige of outstanding scientists is increased.

The Russian government does not believe in weakening its incentive system by high taxes. There are no surtaxes as such, but excess purchasing power, while there are war time scarcities of consumer goods, is absorbed by the very high prices charged for unrationed goods at the government operated "commercial stores," which constitute a kind of official black market.

I found that the work of the institutes of the Academy in Russia even in war time was very largely of a type that we would call fundamental science. The developments in applied science are generally done in special laboratories outside of the Academy.

The Russian government attaches a far greater importance to culture than does our government. Even during the middle of the war in the Siberian town of Novosibersk where the population grew in a few years from 80,000 to 900,000 a large opera house seating 3000 people was constructed even though there was then inadequate housing for war workers. In this opera house performances of opera, concerts, etc., were given which were of the same extraordinarily high quality of those that we saw in Moscow. Similarly, the government sees that books of cultural value are available at low prices and in enormous numbers.

Everywhere among the scientists in Russia I found a deep love for science itself. It was, of course, recognized that science was of great importance because of its applications, but the cultural value of pure science seemed to be considered of equal moment.

As illustrating the importance attached to science I quote from an article, "Science Serves the People" in the *Moscow News.*

> "never before has the scientist been accorded such attention by the state and such esteem by society as in the Soviet Union."
> "the state provides the maximum amenities of life and facilities for work to the scientist and insures a comfortable life to his family after his death."

Now that the war is over the Russian government places A-1 priority on science. The Academy meetings, which lasted two weeks, were attended by 1200 scientists, including over 100 foreign guests. At the meetings it was stressed that the future growth and standard of living of Russia are to be based primarily on pure science and its applications. The lavish entertainment and the banquets, including one in the Kremlin attended by Stalin, and the extraordinary publicity given to the meetings in the Russian newspapers emphasizes the great importance attached to science.

I believe Russia is planning to embark on a program of scientific research and development greater than that contemplated by any other government.

To me it was of particular interest to learn something of the way in which the Russian government carries on its research program. Their reasoning appears to be as follows.

They ask, "who should plan a scientific program? Why of course the scientists. Who are the scientists? All of the most important ones are in the Academy of Sciences." Therefore, the science program is turned over to the Academy and the Academy is held responsible for its success.

The Academy of Sciences of the USSR has 142 regular members and 200 corresponding members. I asked the difference between the regular and corresponding members and was told that the corresponding members get *paid less*. Later in the *Moscow News* I read that the new members of the Academy are *elected by secret ballot* by the members; corresponding members have a "voice" but no vote.

Dr. Joffe, head of the Physical Institute in Leningrad, read a paper before the Academy entitled, "Can Science Be Planned?" He said, "This question has long evoked heated argument and still continues to do so abroad. There are people who complain that the fulfillment of any plan is incompatible with the private initiative of the scientist. He then goes on to say that in Russia where the government renders an all-out aid to scientists it has been found possible to plan scientific work without suffering these disadvantages.

It is clear, however, that Joffe believes in planning only along very general lines. He says, for example, "a plan in science is only a guide to the researcher as to where to begin and what to aim for. There can be no question of its fulfillment the way a factory fulfills its plan; a scientist does not work for the plan but the plan is called upon to help the scientist." He says that research frequently develops along unexpected lines and is then often necessary to alter the original plans or perhaps abandon them completely.

As an illustration of planning in science Joffe says that in May, 1930 he and his colleagues became convinced that "it was essential to begin work on the atomic nucleus. We were all worried, however, because it was the middle of the year and the appropriations for our work had already been made." Although the new researches would require an expenditure of several hundred thousand rubles, Joffe was able in 10 minutes to get the chairman of the Supreme Council of the National Economy to agree to the extra appropriation. "Once started, we have continued work on the atomic nucleus for 15 years as an essential part of our plan."

Comparison of Science Programs of USSR and U.S.A. I am sure we in America would not like Russian methods, and I don't suggest that we adopt them. We must recognize, however, that the methods used in Russia appear to be particularly well adapted to the conditions there and they give every promise of being effective in accomplishing their avowed purposes. It behooves us to find our own American ways of obtaining equally good results. In summarizing I would like to give the following list of characteristics of the Russian system which we need to consider.

> The Russians give the impression of being a strong, rough people with the spirit of pioneers. They are proud of their accomplishments during this war.
>
> They have a remarkable system of incentives.
>
> They have no unemployment.
>
> They have no strikes.

> They have a deep appreciation of pure and applied science and place a high priority on it.
>
> They are planning, I believe, a far more extensive program in science than we are.

In Russia they are frankly incorporating into their communist government the best features of our capitalist system while we are tending to put into our democracy some of the worst features of communism which are now discarded in Russia.

The pioneering spirit in the U. S. shows signs of dying out; we now talk about a 30 hour week—the right to a job. We attach too much importance to security and too little to opportunity.

In 1938 and 1939 I spent some time in France. There, too, labor wanted soft jobs without much work but with increased pay and the people wanted security behind their Maginot Line, but what did they get? Think of Spain, which was once one of the greatest of nations. We should pause and consider very seriously before going too far in discarding the incentives which have brought us to our present position.

The plans for stimulating scientific and industrial progress, and establishing a sound national defense program now before us in the proposed science legislation affords us a remarkable opportunity to retain our leadership and to lay a sound foundation for world wide peace with an increase in the standard of living.

I do not believe that anyone here questions the advisability of establishing comprehensive government support for science and science education. In my opinion the important question before us is how to devise a plan which will provide the necessary incentives to make the plan workable.

Fundamental and Applied Research. In planning a program of this kind we need to distinguish clearly between two distinctly different types of research which we may call fundamental and applied research. The aim of fundamental science is to acquire new basic knowledge. This is inherently unpredictable—discoveries cannot be planned or foreseen.

The aim of applied science is to apply existing knowledge to definite useful ends. A good part of such applied research or development work lies in the field of engineering. Success depends largely upon planning, organization, and financial support.

The cost involved in bringing a project in applied science to a successful conclusion, resulting in the production of some manufactured article, is usually many times greater than the cost of the work that led to the fundamental discoveries upon which the application was based. Thus, in the Bush report, it is stated that in the U. S. A. before the war the annual expenditures in millions of dollars were:

	Basic Science	Applied Science	Percent
Industry	9	180	5
Government	7	50	15
Universities	23	33	70

The main contribution that government can make through the proposed Foundations is to lay better foundations of pure science which can be freely used by all. Such results can best be had in universities. There are two reasons for this: first, the universities provide the ideal environment to stimulate fundamental science and second, the research spirit thus fostered in the university gives an inspiration to the students which is essential for the further growth of both universities and industry.

Universities are usually classed in the Kilgore bill as nonprofit institutions. There are, however, some universities that are keenly aware of the value of patents and which endeavor to arrange their research program so that revenue from patents can support most of their research expenditures. In such cases it is doubtful if the institutions should still be classed as nonprofit organizations.

The proposed Foundations of the Magnuson and Kilgore Bills are also to initiate and support scientific research and development on matters relating to *national defense*. Much of this work will of necessity be in the field of *applied science,* and many of the projects, such as jet propulsion planes or rocket missiles, will be of great magnitude involving the use of heavy equipment and special metals available only in industrial plants.

The nation's interest will then be served by carrying on such projects in industrial laboratories. The experience and know-how of such laboratories may be of decisive importance in the placing of such contracts, just as it often was during the war. Industrial laboratories of this type are built and maintained to serve the industries of which they are part. They are designed to earn a profit and ensure a continued existence to the industry. There is nothing to be ashamed of in making such a profit. In fact, it is a matter of vital public interest that industrial research laboratories can receive incentives through the profits they can make.

These laboratories are not organized to hire themselves out to anyone who wants a job done and merely to receive pay for such services. The *patent provisions of the Kilgore bill,* which puts all ownership of the results of research in the hands of the government, if any small part of the research was paid for by the government, would usually make it impossible for the government to get industrial laboratories to accept contracts for such work. The reason that leads the government to desire contracts for projects of this kind is a need to develop some device of importance in national defense. If the government were to receive all rights for Army and Navy purposes and leave all commercial rights with the industrial laboratory, the government's interests would be protected.

Consider, for example, a case in which an industry has already made great contributions in the development of special steels for jet propulsion turbines that will operate at the exceptionally high temperatures and stresses needed in these devices. Suppose now the laboratory undertakes to do work on a contract with the Foundation and that in the course of this work, a new and greatly improved steel is developed that results in revolutionary improvements. According to the Kilgore Bill the commercial rights for using this alloy for, let us say, a locomotive which uses a gas turbine, would pass to the government and all competitors of the contracting industry would have free use of the improvement. The laboratory would thus have "sold its birth right for a mess of pottage."

There are, however, cases where industrial laboratories might willingly agree that all patent rights should go to the government. For example, in projects such as those involving atomic energy, the rights clearly should reside in the government.

The Kilgore bill, however, attempts to prejudice all such cases. The suggestion has been made that if the laboratory can prove that "undue hardship" has resulted from government ownership of a patent acquired in the course of the work, some kind of an adjustment may be made. I am sure that such a provision would be wholly unacceptable to industry.

It should be the basis of any contract, freely entered into, that both parties contribute to the project. The government gives merely money; the laboratory gives something usually inherently more precious—knowledge, experience, and know-how.

The Magnuson Bill by omitting any provision on patents places the Foundation in the time-tested position of other government agencies, such as the OSRD. For each project a patent clause can be included in the contract that is applicable to the particular case considered. On the basis of the Magnuson bill the Foundation would thus meet no serious patent obstacles in placing its contracts in accord with sound policies of public interest.

A Word on Organization of the Foundation.

The Kilgore bill provides an "in line organization." It aims at an essentially political control of science.

A science program to be efficient must be planned by scientists. It must be based upon cooperation between scientists, administrators, and government. It must furthermore be a long range program. The provisions of the Magnuson Bill are far better. I believe, however, that much is to be gained by placing responsibility upon scientists.

I would, therefore, like to suggest an amendment to Section 3 of the Magnuson Bill by which roughly half the Board members would be chosen from a suitable panel nominated by the National Academy of Sciences.

Chapter Three

WORLD CONTROL OF ATOMIC ENERGY

All scientists seem to agree on the necessity for effective world control of atomic energy. There is now much to justify hope and belief that such control will be attained although the road to it may be long and difficult.

The declaration issued jointly by President Truman and Prime Ministers Attlee and Mackenzie King on November 15 marks the first major step in a constructive program for the solution of the problem of the effective world control of atomic bombs. It is proposed to accomplish this by consolidating and extending the authority of the United Nations Organization so as to establish "a rule of law among nations and to banish the scourge of war from the earth." This goal of world government is to be attained "in separate stages, the successful completion of each one of which will develop the necessary confidence of the world before the next stage is undertaken."

A Commission is to be set up under the UNO to promote a wide exchange of scientists and scientific information and to submit recommendations for the control of atomic energy to the extent necessary to ensure its use only for peaceful purposes, for elimination of atomic weapons from national armaments, and for effective safeguards by way of inspection and other means. It is hoped to create "an atmosphere of reciprocal confidence in which political agreement and cooperation will flourish."

The proposed solution of the problem of the atomic bomb involves essentially a voluntary limitation of sovereignty of powerful nations to the degree necessary to form a world government capable of preventing war. The difficulties are great but the penalty for failure is world disaster.

We have already started an armament race; we are continuing to make bombs and the materials for them. Churchill has stated, "It is agreed that Britain should make atomic bombs with the least possible delay and keep them in suitable safe storage." Molotov, in his report of November 6, said, "We shall have atomic energy and many other things too."

It is unfortunate that a declaration like that of November 15 was not made by Britain, Canada, and the United States at the time that the atomic bombs were dropped in August. To have done so might have prevented or delayed the starting of the armament race. We may hope, however, that the steps that are now planned may lead to a stopping or slowing of the race before it is too late.

In discussing a program for possible attainment of effective world control of atomic energy we must be aware of the difficulties to be overcome and form an estimate of the time available for reaching the goal. I wish to consider particularly the stages that are likely to arise during an armament race and the degree to which these will bring insecurity. This must involve a frank discussion of the characteristics and capabilities of particular nations.

FOUR STAGES OF AN ATOMIC ARMAMENT RACE

In the first stage which now exists we alone have atomic bombs and gradually acquire a stock pile. During this stage we are secure but other nations may feel insecurity to the extent that they are not sure of our intentions.

During the second stage one or more other nations will be making atomic bombs but will not yet have accumulated stock piles sufficient to destroy all of our major cities whereas we will presumably have enough to destroy theirs. Any atomic bomb attack on us would be followed by devastating retaliation; so we still feel moderately secure but other nations are very insecure.

The third stage will arrive when several nations have stock piles of bombs and means for delivering them sufficient to destroy all major enemy cities. Any attack will almost surely be followed by retaliation and will lead to world war. All nations will then be very insecure.

If the race continues long enough, a time will come when one nation, perhaps not the United States, discovers how to make bombs so powerful or so cheaply that it becomes possible not only to destroy the cities of the enemy, but to cover practically the whole country and to kill so much of the population and destroy so many of the bomb launching sites that there can be no effective retaliation. During such a fourth stage the insecurity will become intolerable. A nation which believes itself able to strike without suffering from retaliation and fears that some other nation will soon reach that stage may feel itself justified in launching an attack to prevent future annihilation. A war started under such circumstances is not likely to be a draw. The victor will then have to do what Hitler tried but failed to do—exercise absolute world control—even if originally it had no desire for world conquest.

WHAT NATIONS CAN GET ATOMIC BOMBS AND WHEN?

There are fortunately no easy ways to make atomic bombs. Because of the nature of the chain reaction it is not possible to make bombs much smaller than those already used. The isotope separation needed to produce pure U-235 is extremely costly and must be carried on in very large plants to be economical. The piles used in making plutonium require many tons of materials of extreme purity and the recovery of the small amounts of plutonium that are produced is made difficult by the radioactivity of the products which necessitates remote control of complex chemical processes.

There is now no such thing as "the secret of the atomic bomb." Details of the construction of the bombs and of technical processes of manufacture are now being kept secret but this will not delay the building of atomic bombs by other nations by more than a year or so.

To produce bombs a nation needs a few scientists of high caliber with a large staff of scientifically trained men, well developed industries, skilled technicians, and an efficient organization. Such countries as Sweden and Switzerland might meet these requirements, but the populations are too small to support projects of the magnitude needed unless in the future far easier ways of making bombs are discovered.

A nation will be led to undertake such large projects only by sufficient motivation and incentives. These involve primarily questions of prestige and the intensity of the feeling of insecurity which may develop during an armament race. With small nations prestige and even insecurity are not likely to be sufficiently strong incentives to cause them to engage in large projects since these nations are already accustomed to seeing other nations outstrip them in military preparations.

The high cost of producing atomic bombs is not a serious obstacle for large nations, especially when we consider that these take the place of other weapons which would cost even more. The fact is that atomic bombs, in terms of the damage done, are the cheapest weapons ever devised. The cost of manufacture of a bomb, once the plant is in operation, has been given as roughly $1,000,000, and such a bomb destroys nearly everything within an area of about ten square miles. Over suitable targets the damage done vastly exceeds the cost of the bomb and its delivery. The ratio is at least ten times more favorable than for other types of bombing.

England is undoubtedly the nation, other than the United States, that can first produce atomic bombs. However, because of our understanding of the English people and our confidence in their motives, I doubt if English possession of these bombs will create any strong feeling of insecurity in America.

The next country to make bombs will probably be Russia. Because of the differences in the forms of government between the Soviet Union and the United States and the lack of mutual understanding that has long characterized our relationships, both nations are likely to feel insecurity during an atomic armament race.

Our cooperation with Russia during the war was limited in general to the field of operations. Many of the difficulties that will probably beset the development of effective world control of atomic energy might have been avoided if England and the United States at an early date had invited Russia to participate in the development of the atomic bomb.

A TRIP TO RUSSIA

I was one of sixteen Americans who were invited to attend the 220th anniversary of the founding of the Academy of Sciences of the USSR in Moscow and in Leningrad during June 1945. We had excellent opportunities to observe Russian scientists at work and to learn of the extensive science program that is being planned.

The attendance at the meetings, banquets, etc., held in commemoration of this anniversary was about eleven hundred, including about one hundred and twenty foreign scientists as guests. The fact that such an elaborate program was arranged for a date only about a month after the ending of war in Europe demonstrates that the Soviet Government considers fundamental science to be the foundation upon which they expect to develop their postwar economy. At these meetings it was emphasized that science has always been international in character and this cooperation has been of great benefit to the whole world. The hope was expressed that after the war such cooperation could be extended to other fields.

We visited many of the institutes of the Academy and everywhere found the greatest friendliness and found that all scientific matters could be discussed with complete freedom. We all hoped that the Russian scientists could pay us a return visit.

Much of the work done in the institutes during the war was of a long-range character that would find application only after the war. It had been possible to defer men from military service for such work—something that would have been impossible in the United States. The universities, of which there are now seven hundred ninety, were training more men than ever during the war, but the courses were reduced in length. I was told, as if it constituted an important educational discovery, that ways had been found to train men from the collective farms to become skilled industrial workers in a far shorter time than had previously been thought possible.

Some of the older laboratories had equipment much like that of German or British laboratories of twenty years ago, but some were splendidly equipped and had very skillful machinists, glass blowers, etc. Several large new laboratories were in process of construction and were nearing completion; these are to have excellent equipment. I was shown plans for a new building for the Academy of Sciences about five to ten times larger than the present one.

RUSSIAN PLANNING

The Russians like to plan big projects on a nation-wide scale. The successive five-year plans have been tremendous and successful undertakings. The building of a huge steel industry beyond the Urals long before the war made victory possible. They decided to use mechanical equipment on the farms. The extent to which this was accomplished can be judged by the fact that the Germans captured or destroyed about 200,000 farm tractors, which is about ten times the total number in all Germany.

I was much impressed by the display of Russian-made mechanized equipment in the Victory Parade in Moscow on June 24. The Russian tanks, manufactured in quantity, had shown themselves to be the match of any that Germany had produced and, in the opinion of some experts, they were far better than our own Sherman tanks.

In Moscow I was told that a full sized blast furnace has been operated using oxygen instead of air. A large experimental plant, costing something of the order of $100,000,000, is now nearing completion for the continuous operation of blast furnaces and Bessemer converters. If this work turns out as expected the whole steel industry of Russia will probably be remodeled to adapt it to the use of oxygen, at a cost approximating $2,000,000,000 and with an ultimate large saving in the cost of steel manufacture.

The biggest planned project that the Russians ever undertook was the preparation for war against Germany, extending through the years from 1934 to 1941. The magnitude of this project is demonstrated by the fact that the Russians, with only about 10 percent of their supplies provided through Lend-Lease, were able to drive back the German armies from Stalingrad to Vienna and Berlin. This is all the more remarkable when we consider that the areas invaded by Germany contained about one-half the population and had about one-third of the industrial output of the whole Soviet Union.

The efficiency of the workers and of the administration at the start of large industrial projects has often been very low, but by well planned educational programs, with energy and enthusiasm on the part of the workers, and with a remarkable system of incentives efficiency was usually rapidly raised to a high level. During my short stay in Russia I was particularly impressed by the tremendous emphasis that is placed on incentives.

INCENTIVES IN RUSSIA

In 1931 the Soviet Government adopted the policy that men should serve according to their abilities and be paid in accord with their services to the state. Piecework rates are in effect in industry and on the farms, with high premiums for work done in excess of given quotas. The rationing of food, clothing, housing, etc., is used also to provide incentives. High honors are awarded to workers of exceptional accomplishment.

In the Academy of Sciences one also sees the working of the incentive system. It is a great honor to be an Academician, and with the position there goes a salary and often the use of automobiles, etc. The science program is not planned by political leaders but is turned over to the Academy, whose members are elected by secret ballot, and the Academy is presumably held responsible for the success of the program.

During the war the Russians apparently carried on only a rather small scale program in nuclear physics. For example, Professor Joffe in Leningrad started building a cyclotron before the war but work on this was stopped until this year. I was told that this forty-ton cyclotron is to be completed in December 1945. I believe, however, that now the Russians have already started a large atomic program and that they will carry this out with great skill and ability. We must remember also that in this work they can get great help from German scientists, trained engineers, and technicians.

The rate at which such a program will progress depends largely upon the motivation. Prestige will play a large role. The Russians are proud of their accomplishments during the war and they believe that their success is due to their system of government. The urge to have their own program of atomic energy will be irresistible.

THE EFFECTS OF INSECURITY

Their present feeling of insecurity, which results I believe from our unfortunate handling of the atomic bomb situation, must be a still more powerful incentive.

The Russians realized better than any other nation the state of insecurity in Europe after 1934. At last in May 1945 the war against the aggressors was won and security was attained. All the Russians with whom I came in contact in June expected a long era of peace in which the damage done by the Germans in the devastated areas could be repaired and simultaneously the standard of living could be raised ultimately to a level as high or higher than that in America. Within less than two months the atomic bombs were dropped in Japan.

To understand the effect on the Russians let us consider what American public opinion would now be if we had no atomic bomb project, but, near the end of the war in Europe, atomic bombs had been dropped on Berlin by the Russians without warning. Would our insecurity have been entirely relieved if the Soviet Government a few months later had announced that it held an increasing stock pile of atomic bombs as a "sacred trust"?

If the Russian insecurity rises until it is comparable to that induced by Hitler they might react much as they did then and put 10 percent or more of their national income into a huge atomic energy program while we continue to spend 0.5 percent on bombs and might even dissipate our energies in building a strong but obsolete navy.

RUSSIAN ADVANTAGES IN AN ALL-OUT ATOMIC ARMAMENT RACE

I believe the Russians may reach the second stage, that is, begin to produce atomic bombs, in about three years. Thereafter, however, they might produce bombs faster than we do and so be the first to reach stage 4. In such a race they have certain advantages: they have a large population which can be regimented and can sacrifice standards of living for a long-range defense program; they have a remarkable system of incentives which is increasing their efficiency; they have no unemployment and no strikes; they have already started a more extensive science program than that contemplated by any other government. In Russia they are frankly incorporating into their communistic government some of the best features of our capitalism while we tend to put into our democracy some of the worst features of communism—now discarded in Russia. Thus the efficiency of labor will increase in Russia while in America the stifling of incentives through taxation, the regulation of industry, and unwise labor legislation may impair our capacity to produce. We talk too much about personal security and not enough about opportunity.

I think the actions of the Soviet Union before, during, and after the war have demonstrated that she has no desire for world conquest. She wants primarily security through the destruction of Naziism. We should find grounds for hope and optimism in the fact that the fundamental interests of Russia and the United States are so nearly identical.

We need, however, much better contacts with one another. Edgar Snow, writing recently from Moscow, stated that there are only two hundred sixty Americans in all the Soviet Union. Molotov said on November 6: "Acquaintance with the life of other nations would certainly be of benefit to our people and would broaden their outlook." I hope that this marks the beginning of a new policy which will facilitate travel of Russians to the United States and permit the circulation of American newspapers and magazines in Russia. Another good sign is that English is to be taught to all Russian children.

Changes are taking place rapidly in Russia. Family life is now valued; divorces are hard to get. Efficiency of education has been improved by having separate schools for boys and girls. Churches can be opened wherever the people want them.

The most important change is the abandonment of all plans for foster-ing world revolution—which have so long made communism feared in other countries.

The Russians are shrewd bargainers with many of the characteristics of David Harum. During negotiations one is kept guessing as to their intentions until the time for decision has arrived and a contract is signed. Then they live up to their commitments scrupulously.

I anticipate that before the goal of effective world government is reached we will meet a series of obstacles which will often seem insuperable, but, because what we both seek is in the common interest, the difficulties one by one will clear up unexpectedly.

Above all we will need a spirit of mutual tolerance. Russian and American ideas regarding freedom of speech, freedom of the press, and democracy are often very different. Judging from the actions of the House Committee on Un-American Activities our own ideas on freedom of speech are somewhat fuzzy. The Russians seem to believe that they alone have real democracy—"in other countries in which society is divided between the exploited and the exploiters true democracy is impossible, even though it is proclaimed by constitutions."

Under such circumstances we should not expect to establish our form of democracy in Japan while protesting against democracy of the Russian type in Bulgaria.

By recognizing that Russia has as much right to her form of government as we have to ours we may hope to come to an understanding and agreement on world policies. Persevering along the road toward world government with a spirit of fair play we may in fact ultimately "banish the scourge of war from the earth."

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Chapter Four

SURFACE CHEMISTRY

THE PHENOMENON of adsorption has been known and has been studied for many years. For example, SIR JAMES DEWAR found that charcoal cooled in liquid air was capable of taking up large quantities of such gases as oxygen and nitrogen. This was known to be a surface action depending on the very fine state of division of the charcoal.

The effect of soap in lowering the surface tension of water depends upon the presence of a higher concentration of soap molecules in the surface layer than in the solution.

WILLARD GIBBS proved thermodynamically that there is a general relation between the surface adsorption, the lowering of the surface tension and the concentration of the solution. The equation that he deduced can readily be put in the form

$$\frac{dF}{d\,(\ln p)} = \sigma kT\,, \tag{1}$$

where p is the partial pressure of the vapor of the adsorbed substance in equilibrium with the surface of the liquid, or it may be the partial osmotic pressure of a substance dissolved in the liquid, σ is the number of molecules adsorbed on the surface per unit area, T is the absolute temperature and k is the Boltzmann constant 1.37×10^{-16} erg deg^{-1}, and F, which may be called the spreading force, is given by

$$F = \gamma_0 - \gamma\,, \tag{2}$$

where γ_0 is the surface tension of the pure solvent (in dynes cm^{-1}) and γ is the surface tension of the solution.

The form of GIBBS' equation represented by Eq. (1) is thermodynamically valid if the film is in equilibrium with the 2 volume phases and if the law of ideal gases

$$p = nkT \tag{3}$$

is applicable in the volume phases.

Prior to 1910 many different theories of adsorption had been proposed, but none of them had been very successful. In most of these theories the increased concentration of the adsorbed substance near the surface was thought to be analogous to the retention of the earth's atmosphere by the gravitational attraction of the earth. An adsorbed gas was thus regarded as a kind of miniature atmosphere extending out a short distance from a solid substance. In general such theories were called upon to account only for qualitative aspects of the adsorption of gases on solids. Most of the knowledge of adsorption was empirical. Even GIBBS' law had not been verified experimentally.

When I first began to work in 1909 in an industrial research laboratory (1) (2), I found that the high vacuum technique which had been developed in incandescent lamp factories, especially after the introduction of the tungsten filament lamp, was far more advanced than that which had been used in university laboratories. This new technique seemed to open up wonderful opportunities for the study of chemical reactions on surfaces and of the physical properties of surfaces under well defined conditions. I resolved to try the effect of introducing very small quantities of various gases into a highly evacuated bulb containing a tungsten filament. Since by a McLEOD gauge pressures as low as 10^{-8} atmospheres could be measured, it was possible to observe the disappearance of an amount of gas of less than 0.1 cubic millimeter measured at atmospheric pressure. The use of a tungsten filament presented particular advantages for this could be heated in high vacuum to temperatures of over 3,000°K, so that all impurities could readily be distilled out of the filament. The ease and accuracy with which any desired temperature could be produced and measured was also important.

When a hot body, such as a filament, is in contact with a gas at atmospheric pressure in a glass bulb, the convection currents and the uncertain temperature distribution in the gas are factors which greatly complicate any interpretation of observed phenomena involving the interaction of the filament with the gas.

If the gas, however, is at a pressure as low as 100 baryes,[2] the mean free path of the molecules is many times greater than the diameter of the ordinary tungsten filament. Each molecule which strikes the filament has thus made so many collisions with the bulb since its last collision with the filament, that the effective temperature of the gas in contact with the filament may be taken to be the same as that of the bulb. The disturbing effects of convection currents are then entirely eliminated and the rate of arrival of gas molecules at the surface of the filament can be calculated according to the laws of the kinetic theory of gases. This theory leads to the equation

$$\mu = \frac{p}{(2\pi mkT)^{1/2}}, \qquad (4)$$

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[2] A barye or cgs. unit of pressure, 1 dyne cm^{-2}, is almost exactly 10^{-6} atmospheres.

where μ is the rate of arrival of the gas molecules expressed in molecules cm^{-2} sec^{-1}, and m is the mass of the molecule. By inserting numerical values this equation becomes

$$\mu = 2.65 \times 10^{19} p (MT)^{-1/2} , \qquad (5)$$

where M is the molecular weight of the gas (oxygen = 16) and p is expressed in baryes. By using filaments of small size and bulbs of large size, it was possible to measure experimentally such high rates of disappearance of gas (clean-up) that every molecule that struck the filament disappeared. Under usual conditions, however, the rates of clean-up were far less than this theoretical maximum. The fraction, ε, of all the impinging molecules which reacted on striking the filament could thus be determined.

Working in this way, a systematic study was undertaken of the effects of such gases as oxygen, hydrogen, nitrogen, carbon monoxide, and their mixtures, etc., on filaments of tungsten, carbon, molybdenum and platinum. I shall refer only to those cases where the experiments have thrown light upon the phenomenon of adsorption.

Clean-up of Hydrogen. (3)

When a tungsten filament is heated to temperatures of 1,500°K in hydrogen at about 20 baryes pressure, the hydrogen slowly disappears, the pressure decreasing with time as indicated in curve I of Fig. 1. The pressure falls to a very low value in 10 to 20 minutes. If more hydrogen is introduced, the rate of clean-up is somewhat slower, the pressure decreasing according to curve II. Although analysis shows the residual gas to be pure hydrogen, the clean-up gradually comes to a standstill.

With a bulb containing 2 filaments, it is found that the lighting of the second filament does not cause a recovery in the rate of clean-up. This proves that the gas which disappears is not taken up by the filament itself. By keeping the bulb in liquid air, a greater total amount of clean-up is obtained. Such investigations show that the hydrogen which disappears becomes adsorbed on the surface of the bulb, but that the bulb is capable of adsorbing only a limited amount of hydrogen. This hydrogen adsorbed on the glass is capable of reacting with oxygen at room temperature after the filament has been allowed to cool. The adsorbed hydrogen is therefore in a chemically very active state. It was finally proved that the heated tungsten filament dissociates (4, 5, 6, 7, 8) a small fraction of the incident hydrogen molecules into atoms, and that these atoms, because of their unsaturated chemical nature, exhibit a strong tendency to be adsorbed on glass. These hydrogen atoms, however, are capable of reacting with one another and forming molecules. From this point of view, it should be impossible to hold on the glass more hydrogen than could form a layer one atom deep.

By cooling the bulb in liquid air the adsorption increased. The maximum amount of hydrogen adsorbed on the glass in these experiments was 0.03 mm^3 per cm^2 measured as molecular hydrogen at atmospheric pressure. This corresponds to $\sigma = 1.5 \times 10^{15}$ atoms of hydrogen per cm^2, which is equal to the number of spheres of diameter [3] 2.8 A which can be packed per cm^2 into a close-packed hexagonal lattice. The spacing of the adsorbed atoms is probably determined by the arrangement of the atoms in the underlying glass which provide "elementary spaces" in which atoms can be held. If the average diameter of the atoms of the glass can be assumed to be 2.8 A, the observed maximum amount of adsorbed hydrogen thus agrees well with that to be expected in a monatomic film. If a glass surface saturated with atomic hydrogen at liquid air temperature is allowed to warm up to room temperature, part of the hydrogen escapes as molecular hydrogen; the rest can be driven off at 300°C. Since adsorbed hydrogen atoms probably react on contact to form molecular hydrogen, then experiments indicate that the surface mobility of the adatoms [4] is very small at room temperature.

It was shown that the atomic hydrogen can diffuse long distances through glass tubing at room temperature (but not at liquid air temperature) and can then reduce metallic oxides (9), such as WO_3, CuO, Fe_2O_3, ZnO or PtO_2, and can dissolve in platinum sufficiently to raise its resistance (10). It reacts at room temperature with phosphorus (3) to form PH_3.

Oxygen Films on Tungsten. When a tungsten filament is heated to 1,500°K or more in oxygen at very low pressures, such as 100 baryes or less, the oxygen reacts (11) with the tungsten to form the oxide WO_3 which evaporates from the filament at these temperatures as fast as it is produced, leaving the surface of the filament apparently clean. At temperatures below about 2,200°K the presence of extremely small amounts of oxygen (10^{-6} mm) decreases the electron emission from a tungsten filament to values that range from 10^{-2} to 10^{-5} of that from pure tungsten, depending on the temperature at which the emission is measured. This modification of the properties of the surface must depend upon the presence of a film which contains oxygen. When the filament temperature is high, such as 2,000° or more, the emission returns to a normal tungsten emission as soon as the oxygen is completely consumed or is removed by vaporizing into the bulb a "getter" such as magnesium. If, however, the filament temperature is as low as 1,500°, complete removal of oxygen from the gas phase, even by introducing caesium vapor as a getter, does not remove the oxygen film on the tungsten surface after it has once been formed. This means that the oxygen from such a film does not evaporate appreciably at 1,500°K. Measurements at higher temperatures show that about half of the adsorbed oxygen evaporates in 27 minutes' time at 1,860° and in about 20 seconds at 2,070° (12). From the temperature coefficient at this rate of evaporation it can be concluded that it will take about 3 years at 1,500° to remove half the film by evaporation and that the heat of evaporation is of the order of 160 K. cal. per gram atom.

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[3] Atomic and molecular distances will be given in terms of the Ångström unit 10^{-8} cm, which will hereafter be denoted by A.

[4] J. A. Becker, Trans. Amer. Electrochem. Soc. 55, 153 (1929), has suggested this term for adsorbed atoms.

This heat of evaporation is far greater than the heat of dissociation of oxygen into atoms; so we have very direct evidence that the forces that hold oxygen to a tungsten surface are comparable to the most powerful chemical forces known. This gives reason for believing that the oxygen film which so greatly decreases the electron emission from tungsten consists of a single layer of oxygen atoms which are chemically combined with the underlying tungsten atoms.

The electron emission from the tungsten filament in the presence of oxygen at temperatures below 1,800° is found to be independent of the pressure of oxygen, provided that more than about 10^{-3} barye is present. This must mean that the surface is practically completely covered with oxygen and that an increase in oxygen pressure does not cause the thickness of the layer to increase beyond that of a single layer of atoms.

Curve III in Fig. 1 indicates the way in which the pressure of oxygen in the bulb decreases with time when the tungsten filament is maintained at 1,500°K. The rate of disappearance of the oxygen is proportional to the oxygen pressure and there is no fatigue effect, such as was observed during the clean-up of hydrogen.

Interaction of Oxygen with Hydrogen in Contact with Tungsten Filament. Mixtures of oxygen and hydrogen at low pressures in a bulb containing a tungsten filament behave in an extraordinary manner (See Ref. 13 p. 2271; Ref. 14; and Ref. 15 p. 608). Typical results obtained with a filament temperature of 1,500° are shown in Curves IV and V of Fig. 1. These curves were obtained with a mixture of 3 parts of hydrogen and 5 parts of oxygen. When the filament was lighted, the gas disappeared at exactly the same rate as shown in Curve III when 5 parts of oxygen alone were present. After about 14 minutes practically all of the oxygen had disappeared. This was confirmed by analysis of the residual gas which was found to be pure hydrogen. This hydrogen, however, did not dissociate in the usual way into atoms and disappear by adsorption on the glass walls as shown in Curve I, but the pressure remained practically constant until after about 24 minutes, when the pressure suddenly began to decrease as indicated by Curve V. This Curve V, however, is identical with Curve I, which is characteristic of the clean-up of hydrogen in absence of oxygen. Repeated experiments with different amounts of oxygen and hydrogen prove that hydrogen does not interfere with the clean-up of oxygen but that a minute trace of oxygen of about 10^{-3} barye completely prevents the dissociation of hydrogen into atoms by a tungsten filament at 1,500°K. The oxygen thus acts as a catalytic poison. Experiments of this kind can be used to make quite accurate chemical analyses of mixtures of oxygen and hydrogen.

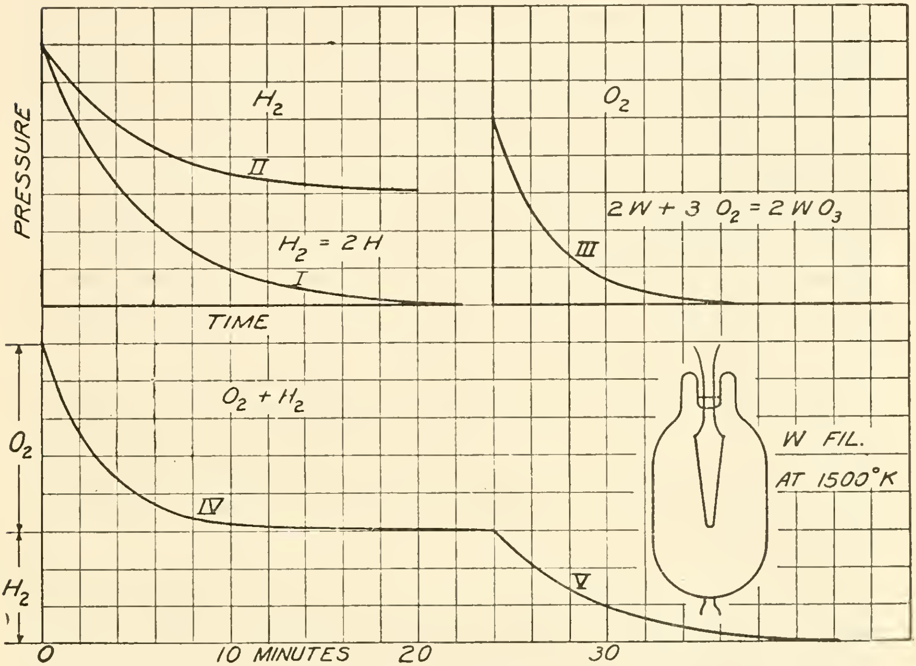

FIG. 1. Clean-up of Hydrogen and Oxygen in a Tungsten Filament lamp.

The fact that a monatomic film of oxygen on tungsten does not react with hydrogen at 1,500° is a striking indication that the oxygen is in a condition far different from that of gaseous oxygen. The results, however, confirm our conclusion that the film consists of oxygen atoms which are chemically saturated by the tungsten atoms with which they are in contact.

In view of the fact that an oxygen film on tungsten at 1,500°K does not evaporate in less than a year, it is remarkable that in the presence of hydrogen the beginning of the hydrogen clean-up (Curve V) is so sharp. Since Curve V is exactly like the lower part of Curve I, it appears that once the hydrogen begins to dissociate, the oxygen is suddenly completely removed from the surface; in other words, hydrogen can remove monatomic oxygen films from the tungsten surface if the amount of oxygen on the surface is less than a definite amount. This probably means that the adsorbed oxygen molecules cannot react with hydrogen atoms directly but can react with hydrogen atoms adsorbed in adjacent spaces on the tungsten surface.

Thorium on Tungsten (16). When a tungsten filament which is made from tungstic oxide containing about 1 percent of ThO_2 is heated to temperatures of 2,800° or more, a minute fraction of the thoria is reduced to metallic thorium. The thoria exists in the filament in the form of minute spherical particles distributed throughout the tungsten crystals and not at the boundaries of crystals. If the filament is then heated for a period of a few minutes at 1900 to 2,000°K, the metallic thorium which has been produced at the higher temperatures diffuses slowly through the crystal grains to the crystal boundaries, then diffuses rapidly along these boundaries to the surface of the filament and then spreads over the surface of the filament by surface migration and forms a monatomic film of adsorbed thorium atoms on the surface of the filament. At 2,000° the rate of evaporation of thorium from the filament is so small that sufficient thorium soon accumulates on the filament to form a nearly complete monatomic film. If the temperature is raised to 2,200 or 2,400°, the rate of evaporation of the thorium from the surface increases so much more rapidly than the rate of arrival from the interior by diffusion, that the actual surface concentration decreases greatly.

These changes in the thorium content of the adsorbed film can be studied by measurements of the electron emission from the filament at a standard low temperature, called the testing temperature, which is chosen so low that neither diffusion to the surface, nor evaporation from the surface, causes appreciable changes in the adsorbed film. A convenient testing temperature is 1,500°. At this temperature the presence of adsorbed thorium on the surface may increase the electron emission as much as 10^5 fold over that from a pure tungsten surface.

Such experiments make it possible to investigate the electrical properties of surface films having known amounts of thorium. On the assumption that each thorium atom on the surface acts as a dipole having a definite dipole moment, it is possible to show that the logarithm of the electron emission should increase linearly with the number of thorium atoms on the surface. The experiments showed that for low concentrations of thorium this relation holds approximately.

There are several indications that the adsorbed film of thorium that is formed by diffusion from the interior never exceeds one atom in thickness.

The Interaction of Carbon Dioxide with Carbon Filaments. If a carbon filament is heated to a temperature above 1,700°K in the presence of carbon dioxide at low pressure, one molecule of carbon monoxide is liberated from every molecule of carbon dioxide (See Ref. 2, p. 1154). If this carbon monoxide is pumped out from the bulb and the filament is then heated to 2,300°K, a volume of carbon monoxide is slowly liberated equal to that originally formed from the dioxide. This proves that each carbon dioxide molecule which comes in contact with the filament and reacts, loses one oxygen atom to the filament and thus produces a carbon monoxide molecule. The oxygen atoms thus transferred to the filament form a monatomic film of oxygen atoms covering the surface, these atoms being chemically combined with the carbon atoms with which they are in contact, presumably by double bonds. This adsorbed film on the filament is very stable at 1,700°, but when heated to 2,300°, the film is destroyed, not by the evaporation of the oxygen atoms, but by the breaking of the bonds between the carbon atoms which are attached to the oxygen and the underlying carbon atoms with which they are in contact. Thus the oxygen escapes as carbon monoxide.

From this point of view we see that we can look upon the adsorbed film on the carbon filament either as consisting of adsorbed oxygen, or as an adsorbed film of oriented carbon monoxide molecules, or as carbonyl radicals which are chemically attached by their carbon atoms to the underlying carbon atoms in the filament. It is to be expected that the properties of the adsorbed film would be very different if it consisted of carbon monoxide molecules attached to the underlying surface through their oxygen atoms. These experiments thus led to the concept that the properties of adsorbed films should in general depend on the orientation of the molecules or radicals in the film. It seemed to the writer (in 1915) that evidence of such orientation could be found among the data on the surface tensions of pure liquids.

Surface Energies of Pure Liquids (17) (18).

If a prism of liquid having a cross section of 1 sq. cm. is divided into 2 parts by an imaginary plane perpendicular to the axis of the prism, and the 2 portions of the liquids are then separated, there has been an increase in the surface of the liquid of 2 sq. cm. The total energy theoretically required per sq. cm. of new surface to bring about this separation may be called the total surface energy γ_0. This is related to the free surface energy γ, which is equivalent to the surface tension of the liquid, by the relation

$$\gamma_0 = \gamma - T\frac{d\gamma}{dT}.$$

By measurements of the surface tension, the surface energy γ_0 can thus be measured. This quantity represents the potential energy of the molecules which form the surface of the liquid (per sq. cm.) in excess of that which the same molecules possess when they are in the interior of the liquid.

In Table I data are given for a few substances which serve to illustrate the interrelation (19) (20) between the orientations of molecules and other properties of liquids. The latent heat of evaporation, λ, which, according to Trouton's Rule, is approximately proportional to the absolute boiling point, T_B, serves as a measure of the energy needed to bring a molecule from the interior of the liquid out into the vapor phase. We have seen that the surface energy γ_0 is the energy per unit area needed to form a surface.

The molecular volume V given in this table is the volume of the liquid divided by the number of molecules. The molecular surface S is the surface of a sphere which has the volume V. The extremely low values of λ, the heat of evaporation, per molecule, for helium and hydrogen, indicate that the forces exerted by these molecules on their neighbours are unusually weak.

TABLE I

SURFACE PROPERTIES OF MOLECULES

Substance Unit =	V Volume A^3	S Surface A^2	T_B Boiling Point ^0K	λ Heat of Evaporation Erg × 10^{-14}	λ/S Erg cm^{-2}	$\gamma_0 =$ Erg cm^{-2}
He	52.	68.	4.3	0.24	0.35	0.59
$H-H$	47.	63.	20.5	1.67	2.7	5.4
$H-OH$	30.	48.	373.	67.	140.	118.
A	47.	63.	88.	11.3	18.	35.3
CH_4	64.	78.	112.	16.3	21.	—
n-C_8H_{18}	266.	200.	398.	56.	28.	50.7
n-$C_8H_{17}OH$	260.	198.	467.	82.	41.5	50.7

This is in accord with the great stability of the electron pair which forms the K shell of atoms and the covalence bond. The diameters of the helium atom and hydrogen molecule given by the kinetic theory from viscosity measurements, viz., 1.9 and 2.4 A, correspond to volumes V of only 3.6 and 7.2 A^3, which are very small compared to the volumes occupied in the liquid. This very open structure of the liquid is again an indication of the weak attractive forces between these molecules.

The effect of replacing one of the hydrogen atoms in the hydrogen molecule by the hydroxyl radical, thus producing water, is to decrease the value of V from 47. to 30., an indication of strong forces acting between the hydroxyl groups which compress the liquid. A better measure of these forces is given by the 40-fold increase in the value of λ from 1.67 to 67. The surface energy γ_0 has been increased 24-fold.

The data for argon illustrate the properties of an atom having a complete electron shell or octet. The fact that in spite of the much larger electron configuration (with a kinetic theory diameter of 2.9) the volume per molecule in the liquid is the same as for hydrogen, shows that the field of force around the molecule is far greater than for hydrogen and helium. The heat of evaporation per unit area λ/S is a very convenient measure of the intensity of this field. With H_2, He and A it is about one-half of the surface energy γ_0.

The data for methane indicate that this molecule has a value of λ/S, about the same as that for argon. This molecule has a completed octet which shares pairs of electrons with hydrogen atoms. Evidently the presence of the hydrogen atoms does not appreciably alter the field of force; the main effect is to raise the molecular volume, thus raising λ and the boiling point T_B almost in proportion to S.

The values for λ/S for the saturated aliphatic hydrocarbons beyond propane are practically constant and equal to 28. The same constancy is shown in the surface energy γ_0. The data for octane shown in the table are typical. The surfaces of the molecules of the higher saturated hydrocarbons are thus very much like those of argon atoms, the effect of the chain formation manifesting itself principally in the increase in λ/S from 18 to 28.

The constancy of λ/S is also an indication that the molecules of the vapors of the higher hydrocarbons are approximately spherical in form. The known flexibility of the chain and the surface energy reduction resulting from the more compact form afford ample explanation of this spherical form.

The effect of substituting a hydrogen atom in octane by a hydroxyl radical is illustrated in the last line of the table by the data for n-Octyl alcohol. There is a small decrease in V paralleling that observed in H_2O, except that now, since each OH group in the liquid cannot be close to many other OH groups, the decrease in volume is considerably less. The large field of force around the OH group is best illustrated by the increase of 26 units in the value of λ. The fact that this increase is less than half of that observed in the change from H_2 to H_2O shows that the OH group in the molecule of the vapor of octyl alcohol is able to bury itself, at least in part, in the approximately spherical molecule.

In spite of the large increase in λ and λ/S in octyl alcohol, the surface energy γ_0 is the same as for octane. This can be explained by the *orientation of the molecules* in the surface layer of octyl alcohol. The great attractive forces exerted by the hydroxyl groups causes them to be drawn down into the interior of the liquid. Thermal agitation tends to counteract this tendency. According to the BOLTZMANN equation the relative distribution of molecules between two regions of differing energy is measured by exp (W/kT), where W is the difference in the energy of the molecule in the two states. Now, judging from a comparison of the values of λ for octane and octyl alcohol, the energy necessary to bring an OH group from a hydrocarbon environment out into free space is at least 26×10^{-14} erg. The energy corresponding to kT at room temperature is about 4×10^{-14} erg. Since W is thus more than 6.5 times as great as this, we may conclude that nearly all of the molecules [all but about exp $(-6.5) = 10^{-3}$] in the surface of octane will be oriented in such a way that the hydroxyl graups do not reach the surface.

We may now understand why the surface energy of octyl alcohol is the same as that of octane. We have previously seen that γ_0 can be determined by the energy needed to separate a prism into two parts. We may conceive of this separation as taking place in two steps. The molecules on the opposite sides of an imaginary dividing plane may first be oriented so that the hydroxyl groups are turned away from this plane, leaving only the hydrocarbon parts of the molecule in contact with the plane surface. The two bodies of liquids are then separated from each other along this plane, which would require only the same energy as for pure octane. Because of the orientation of the molecules, γ_0 thus differs from that of octane only by the amount of energy needed to turn the molecules around in the interior of the liquid, which is probably negligible.

Referring again to Table I we see that a comparison of λ/S with γ_0 affords a measure of the effect of orientation. In general, for molecules with uniform fields of force, λ/S is from 0.5 to 0.55 of the value of γ_0.

When, however, a part of the molecular surface has a much weaker field of force than that of other parts, the surface of the liquid consists principally or wholly of the least active parts, so that γ_0 is lower than normal. Thus for octyl alcohol λ/S is 0.82 of γ_0 while for water it is 1.18, indicating that the water molecule is very unsymmetrical and is strongly oriented at the surface.

At present these illustrations will suffice. In a paper published in 1916 I showed that this theory was applicable to the surface tension of organic liquids in general, including cases of substituted benzene derivatives where the values of γ_0 depend to a marked degree on the relative positions of the substituted groups. Somewhat later W. D. HARKINS and his co-workers investigated large numbers of organic substances in this way and completely demonstrated the importance of orientation of molecules in the surface layer of liquids consisting of unsymmetrical molecules.

Oil Films on Water (18) (21).

When a pure saturated liquid hydrocarbon is placed upon the water, it remains on the surface as a drop or lens which has no effect on the surface tension of the surrounding water. If, however, an insoluble fatty or oily substance, such as the common vegetable and animal oils, is placed upon clean water, it spreads out almost instantly as a thin film over the surface. If the motions of the surface are made visible by dusting the surface with powdered talc, it may be seen that, with a limited amount of oil, the film only spreads out sufficiently to cover a definite area, or at least if the area exceeds a rather definite value, the oil has no effect on the surface tension of the water. A comparison of various insoluble organic substances has proved that the spreading tendency depends upon the presence of certain active groups or radicals in the organic molecule, these being the groups which tend to increase the solubility of organic substances in water. For example, pentane, C_5H_{12}, is practically insoluble in water but amyl alcohol, $C_5H_{11}OH$, is relatively soluble. Thus the OH groups in organic molecules exert strong attractive forces on the OH groups in the water molecules and these manifest themselves by an increase in solubility. Similarly the carboxyl group COOH tends to make the lower fatty acids much more soluble in water than the corresponding hydrocarbons.

Hydrocarbons with high molecular weight such as $C_{18}H_{38}$ are extremely insoluble in water. If the carboxyl group replaces the CH_3 group at the end of the chain $C_{18}H_{38}$, one end of the molecule only tends to dissolve in water, whereas the rest of the molecule still retains the insolubility of the hydrocarbons. By spreading over the surface of the water, molecules of this kind can bring their carboxyl group in contact with the water without separating from one another.

An oil film formed in this way must consist of a single layer of molecules packed closely on the surface layer of the water. If there is a surplus of the fatty acid, as compared with the limited area over which it can spread, the endeavor of the carboxyl groups to come in contact with water causes the molecules to become so crowded at the surface that they stand nearly erect, side by side on the surface. The area occupied by each molecule is thus determined by the cross section of the hydrocarbon chain or by that of the head in contact with water, if this happens to be larger than the cross section of the chain. The thickness of the film is then determined by the length of the hydrocarbon chain.

By dissolving known weights of liquid or solid, oily or fatty substances in a volatile solvent such as hexane, and placing known amounts of these dilute solutions on the water surface, a definite number of molecules can be transferred to the water surface. The oil film can be confined to a given portion of the surface of water in a long tray by a floating strip of paper reaching across the tray. By measuring the forces exerted on the strip of paper, it is possible to measure directly the spreading force F in dynes per cm. exerted by an oil film having a given number of molecules of oil per square cm. of surface. This surface concentration we shall denote by the symbol σ. Such measurements as these, by which F can be expressed as a function of σ and T, give us then the 2-dimensional equation of state of the oil film which corresponds exactly to the 3-dimensional equation of state which characterizes ordinary gases and liquids. In fact, the movable paper strip in these experiments is the equivalent of a piston which compresses the gas in a cylinder.

The oil films observed on water may exist as 2-dimensional solids, liquids or gases. The film on water obtained from stearic acid $C_{17}H_{35} = COOH$ is solid. If it is compressed by a force of 10 dynes per cm. exerted against the paper strip, this solidity is manifested if particles of talc are dusted on to the surface and the effects of air currents directed against the surface are watched. The talc particles do not move freely over the surface; if a strong wind displaces them, they return to their original positions when the wind stops, proving a surface rigidity and elasticity characteristic of solids. Other substances such as cetyl alcohol or oleic acid give films which are liquid, since talc particles circulate freely when small forces are exerted by the wind.

By slightly increasing the area available for these films of saturated fatty acids, it is found that the spreading force decreases very nearly to zero, which proves that these films do not act as 2-dimensional gases but rather as 2-dimensional liquids which have an unmeasurably small 2-dimensional vapor pressure. With myristic acid (22), however, a definite 2-dimensional vapor pressure of about 0.2 dyne cm^{-2} is observed. Still lower fatty acids give typical gaseous films, but they cannot be studied by this method because the films are so easily soluble in water that the force exerted by a moving barrier causes them to go into solution.

Adsorbed Films on Solutions (18) (21). The foregoing method for studying the properties of oil films on water is inapplicable if the film is soluble or is volatile. In such cases measurements must be made in the presence of saturated vapor or saturated solution. GIBBS' equation, Eq. (1), gives us a means of determining the relation between the amount adsorbed on the solution and the spreading force F, in terms of the partial pressure p of the vapor of the adsorbed substance over the liquid or the partial osmotic pressure p of the dissolved substance in the underlying solution. Experimentally F can be measured as the decrease in the surface tension of the pure liquid produced by the presence of the dissolved substance. By the integration of this equation, using the experimentally determined values of F, one can obtain the equation of state of the 2-dimensional film whether this is gaseous or liquid or solid.

For very high or very low surface concentrations, GIBBS' equation takes simple limiting forms. At very low concentrations the molecules in the adsorbed films are so far apart that they exert no appreciable forces on one another. Under such conditions σ, the surface concentration, will be proportional to the volume concentration which in turn is proportional to p. If we solve Eq. (1) on the assumption that σ is proportional to p, we find that it leads to the following equation of state

$$F = \sigma kT\,, \tag{6}$$

which is the 2-dimensional analogue of Eq. (3), the equation of state of an ideal gas, and it may therefore be called an equation of state of an ideal 2-dimensional gas.

The effect of forces acting between the adsorbed molecules is to modify this equation. A 2-dimensional analogue of VAN DER WAALS' equation can be written in the form

$$F = \frac{\sigma kT}{(1-\sigma/\sigma_1)} + a\sigma^2\,, \tag{7}$$

where a and σ_1 are constants.

When the gas phase or the liquid phase contains a relatively high concentration, the concentration of the molecules in the adsorbed film tends to increase to a limiting value σ_1 corresponding to a complete monomolecular adsorbed film such as those that we observed in the study of oil films on water. Although such films show surface elasticity, that is, they are compressible, the forces required to compress the liquid and solid films are so much greater than those required to compress the gaseous film, that the surface compressibility can be neglected as the first approximation, so that we can consider σ_1 to be approximately constant, that is, independent of p and F. Making this substitution in Eq. (1) and integrating, we obtain the following equation which should be applicable for concentrated surface films

$$F = \sigma_1 kT \ln (p/p_0)\,. \tag{8}$$

These two limiting equations are completely in accord with the general relationships found by J. TRAUBE (23). In Eq. (8) p_0 is an integration constant whose value cannot be found from GIBBS' equation.

From the BOLTZMANN equation we can estimate the energy change λ involved in bringing a molecule from the vapor or liquid phase to the surface phase. We thus have

$$\sigma/p = \text{const} \exp (\lambda/kT)\,. \tag{9}$$

TRAUBE found that with molecules of aliphatic compounds having different lengths of hydrocarbon chains, the ratio F/p for dilute solutions (which should be proportional to σ/p) increases about 3-fold for each CH_2. When this is interpreted in accord with GIBBS' and BOLTZMANN equations, we conclude that the energy λ involved in the adsorption of these molecules increases linearly with the length of the chain. This means that each CH_2 group in the molecule must be similarly situated in the surface film. In other words, in these dilute films where there is much free water surface available, the hydrocarbon molecules must lie flat on the surface. With the concentrated films in which σ is constant so that Eq. (8) applies, there is no available free surface of water and the molecules must stand nearly erect on the surface.

These two cases given by Eqs. (6) and (8) are only limiting cases and the complete equation of state for the whole range from dilute to concentrated films would be more complicated, since it must involve the intermediate states between those in which the molecules lie flat on the surface and stand erect on the surface. The experimental difficulties of the accurate measurements of the surface tensions of solutions are such, that relatively little work has been done on the equation of state of these adsorbed films on solutions as compared with the large amount of work done by N. K. ADAM (22) and others on the equations of state of films of insoluble substances on water.

The molecules in adsorbed films on liquids are of course free to move over the surface of the liquid except in so far as the film itself may possess the properties of a solid.

Adsorbed Films on Solids. Adsorbed films on solids may exist in three states corresponding to 2-dimensional gases, liquids or solids. A new factor now appears, however, which was not present in the case of adsorbed films on liquids. The forces exerted by the underlying solid on adsorbed atoms or molecules tend to hold the molecules in definite positions fixed by the lattice of the solid. The solid surface is thus to be looked upon as a type of checkerboard containing definite numbers and arrangements of elementary spaces (13) (24), each of which is capable of holding an adsorbed molecule. To move a molecule from one elementary space to another thus presumably requires something analogous to an activation energy; only those molecules possessing sufficient kinetic energy to pass over a potential barrier can succeed in hopping from one elementary space to another (25). On this basis we should expect a surface mobility at high temperatures which would disappear at low temperatures. The logarithm of the rate of mobility, or the surface diffusion coefficient, should vary linearly with the reciprocal of the absolute temperature and the slope of this line should be proportional to the activation energy.

In general the surface diffusion coefficient increases with σ, for the ability of adatoms to cross the potential barrier is not determined solely by the thermal agitation of the molecules but depends on dF/dσ, since differences in the value of F over the surface contribute to the mobility.

We may thus consider that in general the adatoms on solids move over the surface by hopping between elementary spaces. If the adatoms move nearly independently of one another, so that they migrate freely on to all unoccupied portions of the surface, the adsorbed films can be regarded as a 2-dimensional gas in spite of the fact that the atoms tend to occupy definite positions. Such films constitute a 2-dimensional crystalline gas, the crystalline character being imparted by the underlying lattice. If attractive forces exist between the adatoms which are sufficiently strong to cause them to form a definite 2-dimensional condensed phase in equilibrium with a 2-dimensional vapor phase, we clearly have to do also with a 2-dimensional solid or liquid. If the mobility is high, this condensed film may have properties characteristic of liquids; with no mobility at lower temperatures, the conditions will be analogous to that of a 2-dimensional glass. A 2-dimensional solid analogous to ordinary 3-dimensional solids would exist only if the forces exerted by the adatoms on each other can keep them from slipping past one another.

Condensation-Evaporation Theory of Adsorption on Solids. When molecules of a gas in contact with a solid impinge individually on the solid, they may either condense or may rebound from the solid as though elastically reflected. Those molecules that condense may subsequently evaporate. There is much theoretical and experimental evidence that a true reflection of molecules under these conditions is a rather abnormal occurrence, although the specular reflection of molecular rays from certain crystalline surfaces shows that it sometimes exists. In the great majority of cases, however, the observed phenomena indicate that the larger part of all incident molecules condense on the surface and reach thermal equilibrium with it before they evaporate (26) (27). With such gases as hydrogen and helium accommodation coefficients materially less than unity have been found. In general these occur with gases striking solids at such temperatures that the rate of evaporation may be assumed to be so high that the life of the condensed molecule is of the order of 10^{-13} seconds, which is about the time required for a molecule to perform a single thermal oscillation on the surface. Under these conditions it is not surprising that thermal equilibrium is not reached.

When the rate at which molecules impinge on the surface is μ, as given by Eq. (4), and ν is the rate at which they evaporate (molecules cm^{-2} sec^{-1}), then the rate at which they accumulate on the surface is given by

$$\frac{d\sigma}{dt} = \alpha\mu - \nu, \tag{10}$$

where α, the condensation coefficient, in the majority of cases is equal to unity, but in any case can never exceed unity. The rate of evaporation ν is in general dependent on the temperature and on σ, the surface concentration. Of course it also depends on the nature of the solid surface on which adsorption occurs. If the surface is strictly homogeneous, ν may be a function of σ and T only for a given surface, but it may be possible that different portions of the surface are capable of exerting different forces on adatoms, so that ν and σ may not be uniform over the surface.

In a stationary state when σ is not changing with time, the general condition that must be fulfilled is

$$\alpha\mu = \nu\,, \tag{11}$$

If we divide the rate of evaporation ν by σ, the number of atoms per square cm., we obtain the average probability per second for the evaporation of the individual atoms. The reciprocal of this, τ, is thus the average life of an adatom on the surface. Thus we have

$$\tau = \sigma/\nu. \tag{12}$$

This time lag that exists between the condensation and the evaporation of adatoms may thus be looked upon as the fundamental cause of the adsorption of gases on solid surfaces.

In general ν should increase rapidly with temperature like the vapor pressure of substances. Thus the logarithm of ν should increase approximately linearly when plotted against the reciprocal of the absolute temperature, and the slope of this line is proportional to the heat of evaporation and is a measure of the magnitude of the forces by which the adatoms are held on the surface. Thus ν should be approximately given by an equation of the type

$$\nu = \text{const. } \exp\left(-\lambda/kT\right), \tag{13}$$

where λ is a measure of the energy required to remove an adatom from the surface. The reason for the large variations of ν for different substances is due mainly to variations of λ rather than to differences (28) in the constant factor in Eq. (13). This is indicated by such approximate laws as TROUTON'S rule.

The forces acting between atoms and molecules are normally of extremely short range (27) (29), so that the forces acting on an adatom, which determine the magnitude of λ, and therefore of ν, depend mainly upon the atoms with which any given adatom is in contact. When the gas pressure is raised or the temperature is lowered so that σ increases to such a point that there is no longer room for any additional molecules in the first layer in contact with the solid, a still further increase in σ would require that a large number of adatoms must be contained in a second layer. Now these adatoms in the second layer cannot be in *contact* with the solid surface on which the primary adsorption occurs, and therefore for these atoms λ_2 should differ from the value of λ_1 that applies to the adatoms in the first layer. Since λ occurs in the exponent of Eq. (13), a relatively small change in λ is sufficient to cause a marked difference in the value of ν.

Thus when the adsorbed substance is not nearly identical in its properties with the substance on which adsorption occurs, we should expect the value of ν for atoms in the first and atoms in the second layer to be greatly different from one another. Naturally two cases may arise: ν_2 may be either greater or less than ν_1. (Ref. 28, pp. 2811 and 2815.)

Case 1. $\nu_2 < \nu_1$. If ν_2 is less than ν_1, the atoms in the second layer are held by stronger forces to those in the first layer than these latter are by the atoms of the underlying solid. There is therefore a tendency for the atoms in the first layer to form clusters and on these clusters the second and third, etc., layers begin to form long before the whole of the first layer is covered (27). Such phenomena are of common occurrence. For example, when mercury, cadmium or iodine is vaporized in vacuum and is condensed on a glass surface, at a not too low temperature, discrete crystals of the condensed substances form on the glass. This is a direct indication that these atoms exert greater forces on one another than they do on the underlying glass.

If the glass surface is maintained at a temperature so high that these nuclei do not form, then the glass surface *appears* to reflect all the incident atoms, for they evaporate from the glass surface far more rapidly than they do from a cadmium surface at the same temperature. Such observations were made by R. W. Wood, who attempted to explain them by a large reflection coefficient. He believed that experiments indicated that molecules of mercury incident at low pressures on cold glass surfaces were completely reflected at temperatures above −90°C, but were completely condensed below that temperature.

From our present viewpoint such a critical temperature has nothing to do with a true reflection but is dependent on the fact that with a given stream of mercury or cadmium atoms there is a definite temperature below which evaporation of the individual adatoms cannot take place fast enough to prevent accumulation sufficient to form a monatomic film, so that all further evaporation at these low temperatures ceases. Experiments show conclusively that at all temperatures the mercury atoms condense, but that, if the temperature conditions are favorable, single atoms re-evaporate from the glass at fairly low temperatures.

It is evident therefore that those cases in which ν_2 is less than ν_1 are characterized by the growth of crystals from nuclei and do not lead to the formation of monomolecular films but rather to discrete crystal particles.

Case 2. $\nu_2 > \nu_1$. In this case, as the pressure is gradually raised or the temperature is lowered, σ increases until a monomolecular film is formed, but it then takes a considerable decrease in temperature or increase in pressure before a second layer begins to form. These conditions therefore commonly lead to the formation of films which do not exceed a molecule in thickness over a wide range of experimental conditions. This case therefore is characterized by typical adsorbed films.

Adsorption Isotherms. The fundamental equation governing the amount of adsorbed substances on a solid surface is given by Eq. (11). To put this into a definite form relating the pressure p of the external gas and σ, the surface concentration, we need only to be able to express α and ν as functions of σ and T. The functional relation of ν to σ depends not only on the forces exerted by the underlying solid, but on the forces acting between adatoms. Furthermore we must consider that the incident molecules corresponding to μ cannot all go directly into elementary spaces on the bare surface, but many of them will make their first contact at places already occupied by adatoms. An important aspect of the problem of the adsorption isotherm is the determination of the manner in which these incident atoms find places in the first layer. Many atoms may temporarily be forced to occupy places in the second layer from which they can either evaporate at a much higher rate than from the first layer, or may migrate until they drop into positions in the first layer.

It is natural under these conditions to make assumptions which are as simple as possible and to see whether the resulting equations can find a field of application (24). If the adatoms do not exert appreciable forces on one another, we may thus assume that the life of τ of each one is independent of the presence of other atoms on the surface. Thus by Eq. (12) ν is proportional to σ.

Instead of dealing with the surface concentration of σ it is often convenient to use the covering fraction Θ defined by

$$\Theta = \sigma/\sigma_1, \tag{14}$$

where σ_1 is the surface concentration in a complete monomolecular film.

Thus we may put

$$\nu = \nu_1 \Theta, \tag{15}$$

where ν_1 represents the rate of evaporation from a completely covered surface.

When molecules incident on the surface strike a part which is unoccupied by other adatoms, we may assume that the fraction α_0 condenses. The fraction of such surface which is bare may be represented by $1 - \Theta$.

Therefore the number of incident atoms which go directly into the first layer may be put equal to α_0 $(1-\Theta)$ μ. The fate of the other incident atoms, viz., those that first strike adsorbed atoms, will depend on many factors, some of which we shall discuss later. A very simple, although not very probable, assumption is that all these atoms reevaporate so fast that they do not have opportunities to find positions in the first layer. On these assumptions we find

$$\alpha\mu = \alpha_0 (1 - \Theta) \mu \; . \tag{16}$$

Substituting this and Eq. (15) into Eq. (11) and solving for Θ, we obtain the following simple adsorption isotherm,

$$\Theta = \frac{\alpha_0 \mu}{\nu_1 + \alpha_0 \mu} . \tag{17}$$

This equation has been found to apply with reasonable accuracy to a suprisingly large number of cases of adsorption on plane surfaces. Considering the nature of the simplifying assumptions made in its derivation, it should of course not be looked upon as a general equation for the adsorption isotherm. The cases where this equation is most likely to apply are those in which the adsorption occurs only in elementary spaces which are so far separated from one another that the adatoms in the separate spaces do not exert appreciable forces on one another. This can justify the assumption of Eq. (15). Also in this case the condensation may reasonably occur according to Eq. (16), because if a given space is occupied, which has a probability proportional to Θ, the incident atom cannot merely slip into an adjacent elementary space but must fall on to an area on which it is held with so little force that it evaporates before it can move into any vacant elementary space. These assumptions will give us an equation like Eq. (17) except that the significance of Θ and of the coefficient α_0 is somewhat modified.

Recent experiments have shown that in the mechanism of condensation mobility plays an important part (30). Thus in general an incident molecule striking a surface already covered may be assumed to move an appreciable distance before finally settling into a position in the first layer. Certainly if the surface is homogeneous so that all parts of it are available for adsorption, an incident molecule striking an isolated adsorbed molecule can hardly be regarded as being even temporarily in a second layer. Such an atom will slip into a position in the first layer before having any occasion to rebound or evaporate from the surface. An atom cannot be in a second layer even temporarily unless it is supported by at least three or more often four atoms in the underlying layer. Even if there is no mobility, the probability that an incident atom could occupy a place in the second layer would be proportional to Θ^n, where n is at least as great as 3 or 4. If the rate of evaporation is very high, we might expect these atoms to evaporate before finding places in the first layer. On this basis, therefore, instead of Eq. (16), the expression for the rate of arrival of atoms in the first layer should be

$$\alpha\mu = \alpha_0 (1 - \Theta^n)\,\mu\,. \tag{18}$$

Some experiments were made to test the reasonableness of these conclusions. The bottom of a tray was covered with steel balls (3/8 inch diameter) closely packed into a square lattice and cemented into position. This surface thus possessed many of the features of a homogeneous crystal surface, the steel balls corresponding to the individual atoms. When other balls of the same size were thrown on to the surface, they occupied definite elementary spaces, each being in contact with four underlying balls. The number of such elementary spaces (except for an edge correction) was the same as the number of balls which were cemented into place (zero layer). A large number of balls, sufficient to cover the fraction Θ of the available spaces, was placed in the tray (in first layer) and the tray was shaken to give a random distribution. A small number of additional balls was then dropped at random from a height of 5 cm. to the surface, and the number of these which went into the second layer was counted. It was found that the probability P that a given incident ball would occupy a position in the second layer was quite accurately given by

$$P = \Theta^{4.5}\,. \tag{19}$$

The fraction of the incident balls finding positions in the first layer was thus $1-\Theta^{4.5}$. A comparison of this with Eq. (18) gives a value of $n=4.5$. The reason that n is greater than 4, the number of underlying atoms, is probably that the kinetic energy of the balls causes some of them to roll from their positions of first contact.

Applying these results to adsorption, we should expect that, until Θ is very close to unity, all atoms incident on the surface should reach positions in the first layer without any opportunity of evaporation or reflection, even if the evaporation rate in the second layer is very high.

Effect of Forces Acting between Adatoms (28). The fact that 2 adatoms cannot occupy the same elementary space at the same time must mean that they exert repulsive forces on one another. This will manifest itself in the equation of state of the adsorbed atoms by a factor such as the $1-\Theta$ in the denominator of the first term of the second member of Eq. (7). This means that the spreading force tends to rise indefinitely as Θ approaches the value unity. Combining this equation of state with GIBBS' equation, and assuming $\alpha = 1$, we obtain for an adsorption isotherm the equation

$$\ln(\nu/\Theta) = \ln[1/(1-\Theta)] + 1/(1-\Theta) + \text{const.} \tag{20}$$

Thus we see that the rate of evaporation should increase indefinitely as Θ approaches unity. It is just this effect which limits the amount of material in typical adsorbed films on liquids or solids to that contained in a monomolecular layer.

The forces holding adatoms on the surface in characteristic cases of adsorption are usually far greater than those acting between adatoms. If this were not the case, we would be dealing normally with the case in which ν_2 is less than ν_1, so that we would not have adsorbed films but crystal nuclei. The effect of these strong forces originating from the underlying surface is to polarize the adatoms. If these are all of one kind, they thus tend to become similarly oriented dipoles which repel one another with a force varying inversely as the fourth power of the distance between them. There may also be attractive forces of the VAN DER WAAL'S type, but these will vary with a much higher power of the distance. The dipole forces will have a range of action far greater than other forces involved. A knowledge of these factors which are probably important in most cases of adsorption can best be acquired by a detailed study of some one example in which quantitative determinations of all the factors are possible. The example that I have chosen for this purpose is that of adsorption of caesium vapor on tungsten, for in this case we can measure with great precision the surface concentration σ as well as the rates of evaporation ν of atoms, of ions, and of electrons (30). Thus we are able to express these values of ν_a, ν_p and ν_e as functions of Θ and T. These measurements enable us not only to determine the forces acting between the adatoms but also to determine the electrical properties of the adsorbed films.

Caesium Films on Tungsten. The ionizing potential of caesium is 3.9 volts, which is lower than that of any other chemical element. The heat of evaporation of electrons from tungsten corresponds to 4.6 volts. Thus the energy necessary to detach an electron from a caesium atom is 0.7 volts less than that necessary to pull an electron out of metallic tungsten. It is therefore not surprising that experiments (31) (32) show that every caesium atom which strikes a tungsten filament at high temperature loses its electron and escapes as a caesium ion. The electric current that thus flows from the tungsten is a quantitative measure of the number of atoms of caesium that strike the filament. Since currents of 10^{-17} amps. can be measured by an electrometer, it thus becomes possible to detect a pressure of caesium vapor so low that only 100 caesium atoms per second strike the surface of a filament.

The escape of the caesium ions from the tungsten surface is an evaporation phenomenon. If the temperature is below about 1,100°K, the rate of evaporation of the ions may be so low that it does not keep pace with the rate at which the atoms arrive, so that there is an accumulation of adsorbed caesium on the surface. As a matter of fact, the rate of evaporation of the adsorbed caesium from the surface at a thousand degrees is about the same as that from a surface of metallic caesium at room temperature (300°K). Thus from TROUTON's Rule we should expect the heat of evaporation of caesium adatoms to be about three times as great as the heat of evaporation of caesium itself.

Such large forces between the adsorbed caesium atoms and the underlying tungsten surface are to be expected as a result of the fact that the caesium tends to lose its electron when close to the tungsten surface. Thus the positively charged caesium ion induces into the conducting tungsten surface a negative charge, which exerts a force of attraction on the ion (the «image force») equal to $e^2/4x^2$, where x is the distance of the ion from the surface. This image force is of ample magnitude to account for the strong forces holding caesium on tungsten.

If a thoriated tungsten filament is used, and this is given the special heat treatment required to bring a complete monatomic film of thorium to the surface, the heat of evaporation of electrons falls to about 3 volts, which is 0.9 of a volt lower than the ionizing potential of caesium. In accord with this fact the experiments show that caesium atoms are not converted into ions by an activated thoriated filament, nor is there any observable tendency for the caesium to become adsorbed on the filament.

If, with a pure tungsten filament in presence of caesium vapor, the temperature is maintained low enough to permit an adsorbed film of caesium to be formed, the positively charged adatoms, which cause a positive contact potential against the pure tungsten surface, have the effect of lowering the heat of evaporation of the electrons. When such an amount of caesium is present on the surface that the heat of evaporation is materially below 3.9 volts, the tendency of the filament to rob incoming caesium atoms of their electrons and thus allow them to escape as ions is lost. This means that ν_p, the rate of evaporation of ions, becomes very small as Θ, the fraction of the surface covered by caesium atoms, increases.

At temperatures of about 700°K, in presence of caesium vapor saturated at room temperature (pressure about 10^{-9} atmospheres), Θ increases to approximately 0.7 and the heat of evaporation has then been lowered to such a point that the electron emission is 10^{22} times greater than that of a clean tungsten filament at the same temperature.

Within the last three years, Dr. J. B. TAYLOR and I have made a detailed study (28) (30) of the rates of evaporation of atoms, ions and electrons from these caesium films on tungsten as functions of Θ and T. In order to measure Θ, a method was devised for determining σ, the number of adsorbed atoms per square cm. of tungsten surface. Two methods were found. When Θ is less than 0.08, a sudden heating or flashing of the filament at temperatures above 1,300° causes every caesium adatom to escape from the filament as an ion so that the ballistic kick measured with the galvanometer gives directly the value of σ. The second method, which is applicable at any values of σ (even those corresponding to polyatomic layers), involves the evaporation of the adatoms as atoms, in the presence of a retarding field which prevents the escape of ions. This burst of atoms falls on a parallel neighbouring tungsten filament heated above 1,300° from which these atoms escape as ions. The ballistic kick of current from this second filament thus measures σ on the first filament. We call this the 2-filament method of measuring σ.

The measurements of σ showed that as the caesium pressure is increased or the filament temperature lowered, σ increases to a definite limiting value of σ_1 which is 4.8×10^{14} atoms per square cm. of apparent filament surface. A study of the crystal habits of tungsten has shown that the surface lattice of surfaces etched by evaporation contains 1.425×10^{15} atoms per square cm. Since the diameter of the caesium atoms is almost exactly twice that of tungsten, and because of the tendency of the adatoms under the strong forces exerted by the tungsten, to occupy definite elementary spaces on the surface, we conclude that the maximum number of caesium adatoms is one quarter the number of tungsten atoms and therefore the true value of σ_1 is 3.563×10^{14} atoms per square cm. Comparing this with the observed or apparent value of σ_1 it appears that the true surface of the tungsten filament is 1.347 times the apparent surface, this difference being due to the slight etching of the filament surface by evaporation at high temperatures.

A study of transient states during which Θ increases or decreases with time has proved conclusively that the phenomenon of condensation or evaporation go on independently of one another, the condensation being dependent on μ, while the evaporation ν is strictly a function of Θ and T only, and does not depend upon the way the surface film has been formed.

The experiments show that within the accuracy of the experiments (about 0.5%) the condensation coefficient α is always equal to unity even when Θ is as great as 0.98. This proves that the incident atoms, which under these conditions must nearly all strike adatoms, can slide around in a second layer until they find positions in the first layer. The experiments prove, however, that the number of atoms which exist at any time in the second layer is extremely minute, of the order of 10^{-7}. The atoms in the second layer possess very high surface mobility.

The rate of evaporation of atoms ν_a increases at any given temperature extremely rapidly as Θ increases. Thus at 1,000°K an increase of Θ from 0.1 to 0.9 causes a 10^{11}-fold increase in ν_a. This indicates very strong repulsive forces between the adatoms in agreement with the fact that these adatoms tend to be positively charged as indicated by the effect of the film in increasing the electron emission. It has been possible to develop this relationship between ν_a and ν_e into a quantitative theory.

A single caesium adatom on a tungsten surface may be regarded as an ion held to the metal by its image force. The image and the ion thus constitute a dipole, having an electric moment M, oriented with its axis perpendicular to the surface. Because of the strong electric fields close to the ion when it is adsorbed on the surface, we should expect the conduction electrons in the metal to be drawn towards the ion so that the dipole moment should be considerably less than we would calculate for a caesium ion at a distance from an ideal metal surface equal to its radius. The experimental values of M have actually been found to be 16.2×10^{-18}, whereas we calculate 25×10^{-18} for a spherical caesium ion in contact with an ideal conducting plane.

The force f between two such adion dipoles is given by

$$f = (3/2)\, M^2/r^4, \tag{21}$$

where r is the distance between the adions.

We may now work out the equation of state of the adsorbed caesium films in terms of these forces by means of CLAUSIUS' virial equation which for surfaces takes the form

$$F = \sigma kT + (1/4)\, \sigma \Sigma (rf), \tag{22}$$

where the summation is to extend over all adatoms which act on any one adatom. The forces f are of two kinds: first, the long range forces which correspond to the dipole repulsion given by Eq. (21), and second, the short range forces acting between atoms in contact which prevent any two from occupying a single elementary space at the same time. These short range forces may be taken into account by dividing the second member of Eq. (6) by $(1 - \Theta)$, as has already been done in Eq. (7). In this way by an integration process it has been possible to derive the general equation of state for adsorbed atoms which repel as dipoles. This equation is

$$F = \sigma kT/(1 - \Theta) + 3.34\, \sigma^{5/2} M^2 + 1.53 \times 10^{-5} \sigma^2 T^{1/3} M^{4/3} I, \tag{23}$$

where I is an integral whose numerical value can never exceed 0.89 and which can be obtained from tables and curves from the value of M, σ and σ_1.

The spreading force F calculated in this way cannot be measured directly for a solid surface but it can be related to the rate of evaporation ν_a by means of GIBBS' equation

$$\frac{dF}{d \ln \nu_a} = \sigma kT. \tag{24}$$

By substituting in this equation the values of F from Eq. (23), ν_a can be calculated in terms of M. Actually we have reversed the process. From the experimentally determined values of ν_a as functions of σ and T, we have calculated F by Eq. (24) and from these by Eq. (23) have obtained M. These values of M are found to be functions of σ but are not appreciably dependent on T, although a slight dependence is indicated by the form of Eq. (23).

A test of this theory can be made since the values of M obtained from ν_a may be compared with values of M obtained from the contact potential which may in turn be obtained from measurements of ν_e. The contact potential V of the surface covered with an adsorbed film as compared with that of a pure metal surface is given by

$$V = 2\pi\sigma M. \tag{25}$$

Furthermore the electron emission ν_e is related to the contact potential V by the Boltzmann equation

$$\nu_e/\nu_w = \exp(Ve/kT), \tag{26}$$

where ν_w is the electron emission from pure tungsten at the same temperature. The full line curve in Fig. 2 gives values of V calculated by Eq. (25) from M as determined from ν_a. The points shown by small circles represent values of V obtained from ν_a by Eq. (26).

The values of V obtained by these two independent methods agree nearly perfectly when $\Theta < 0.5$. The deviations at higher values of Θ seem to indicate that for high values of Θ the short range forces are somewhat greater than those given by the factor $1 - \Theta$, the denominator of the first term of the second member of Eq. (23). Calculation shows that for a value of $\Theta = 0.75$, that part of the spreading force which is due to the short range forces is actually 45 percent greater than is given by the first term in the second member of Eq. (23).

It is also possible to calculate the contact potential from data on ν_p, the rate of evaporation of ions from the surface. The values of ν_a, ν_e and ν_p must be so related to one another that they give concentrations of atoms, electrons and ions in the vapor space near the filament which agree with the thermodynamical requirement for equilibrium among these particles. We may thus put

$$n_e n_p / n_a = K, \tag{27}$$

where K is the equilibrium constant that can be determined from the ionizing potential in accordance with the Saha equation. When this is done, and we combine with the Boltzmann equation and the Dushman equation for the electron emission from tungsten, we obtain

$$\ln (2\nu_p) = \ln \nu_a + (e/kT)(V_w - V_i - V), \qquad (28)$$

where V_i is the ionizing potential of caesium, and V_w is the heat of evaporation of electrons from tungsten. The values of the contact potential V calculated from ν_p in this way are indicated in Fig. 2 by crosses. These points lie on the curve obtained from ν_a.

This agreement of the values of V obtained by these three methods shows that our theory gives a complete account of the electrical and chemical properties of moderately dilute adsorbed films of caesium on tungsten. It proves also that the surface of these tungsten filaments was essentially homogeneous, so that the probability of evaporation of any adatom or adion was independent of the position of the atoms on the surface and was determined wholly from the value of σ at that point.

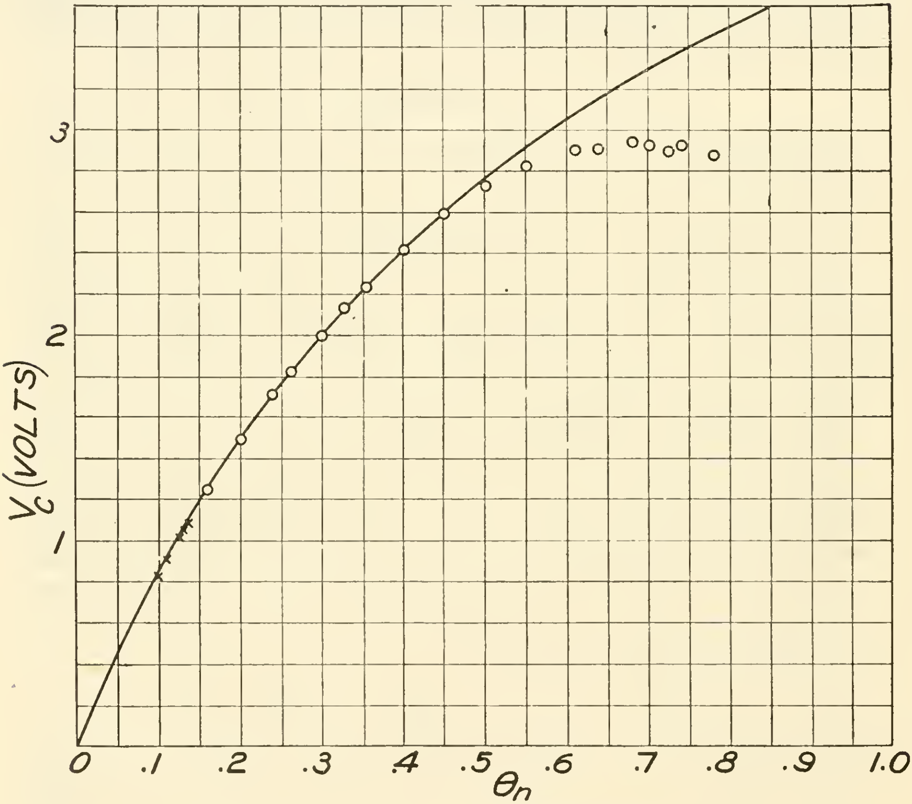

Fig. 2. Contact Potential of Caesium Films on Tungsten against Clean Tungsten.

The experiments showed, however, that this conclusion, although true for over 99 percent of the surface, did not hold exactly. Deviations at very low values of Θ indicated that about 0.5 percent of the surface consisted of what we may call active spots which adsorbed caesium far more strongly than the rest of the surface, so that the heat of evaporation of these areas was about 37 percent greater than that for atoms on the normal part of the surface. Experiments also showed that adsorption on this part of the surface was of the type indicated by Eq. (17): the simple type of adsorption isotherm. This means that the atoms adsorbed in the active areas did not exert appreciable forces on one another. Evidently the active spots consist of separated elementary spaces distributed over the surface, probably near grain boundaries or at steps in the crystal faces.

A variation of the dipole moment M with σ results from the depolarizing effect of neighbouring dipoles. The electric fields due to these dipoles can be calculated by an integration process similar to that used in calculation of F, and are of the order of 5×10^7 volts cm^{-1}.

When a tungsten filament is heated to about 1,100° in caesium vapor and there is an accelerating field drawing ions from its surface, two coexistent surface phases may occur. For one of these Θ is about 0.15, while in the other it is very close to zero. The atoms that strike the less concentrated phase evaporate as ions, while those that strike the concentrated phase evaporate as atoms. The phase boundary is perfectly stable and stationary at a definite temperature in the presence of a given pressure of caesium. If the temperature is raised slightly, the phase boundary moves towards the concentrated phase, so that the whole filament gradually becomes bare; a lowering of the temperature causes the whole surface to become covered with the concentrated phase. A detailed analysis of the mechanism at the boundary between the phases which involves diffusion from one phase to the other, makes it possible to measure the surface diffusion coefficient D. Results have shown that

$$\log D = -0.70 - 3060/T.$$

From the temperature coefficient of D it can be calculated that the surface diffusion activation energy is about 0.6 volts. This means that between each of the elementary spaces there is a potential barrier of the height of 0.6 volts over which the adatoms must hop in order to migrate over the surface.

The experimental methods involved in these studies of caesium films on tungsten are capable of very great accuracy and sensitiveness, so that they seem to offer a rich field for the detailed study of adsorption phenomena. Dr. Taylor and I are continuing work in this field. We are planning to make accurate comparisons between the properties of films of adsorbed caesium, rubidium and potassium. We have developed a method of introducing definite small amounts of oxygen by diffusion through a heated silver tube. In this way known numbers of oxygen atoms may be placed on the surface of a tungsten filament thus forming negative dipoles. These attract the positive caesium dipoles which tend to form clusters around them, forming a kind of 2-dimensional colloidal distribution of caesium. We hope by the detailed study of such systems to learn the effects not only of repulsive but also of attractive forces between adatoms. Experiments are also in progress to study the adsorption of caesium on tungsten surfaces containing known numbers of adsorbed thorium atoms.

In such ways as these, together with the methods involving the spreading of oil films on water, it becomes possible to determine the equations of states of 2-dimensional gases, with nearly the same degree of accuracy as in the case of 3-dimensionals, but with the further advantage that the conditions are especially favorable for the determination of the mechanism of all of the processes involved.

Types of Adsorption.

The classical kinetic theory of gases, as for example in the treatment of viscosity by SUTHERLAND and of the continuity of the transition from gas to liquid by VAN DER WAALS, led to the recognition of attractive forces between molecules at large distances and of strong repulsive forces at short distances. The chemist has long known that exceptionally large attractive and repulsive forces are associated with the chemical union between adjacent atoms, which he represents by the valence bond (primary valence) and that weaker forces, which he has called secondary valence forces, usually correspond to other types of chemical combinations. The physicist has studied the forces between charged particles, such as ions and dipoles, and more recently has discovered the interchange forces, which are best explained in terms of quantum mechanics.

In the structure of matter there can be no fundamental distinction between chemical and physical forces: it has been customary to call a force *chemical,* when it is more familiar to chemists, and to call the same force *physical,* when the physicist discovers an explanation of it. There are also usually no sharp dividing lines between attractive and repulsive forces or between the various kinds of attractive or repulsive forces. Nevertheless a recognition of various types of forces responsible for the stability of matter proves useful in classifying natural phenomena. Thus in a qualitative way we may consider the following types of forces (29):

(1) COULOMB forces between ions or ions and electrons varying with $1/r^2$ where r is the distance between ions. The best examples of these forces are in salt-like substances.

(2) Forces between dipoles which vary with $1/r^4$ and depend on the orientation of the dipole.

(3) Valence forces, associated with the sharing of electrons between atoms.

(4) VAN DER WAALS' attractive forces, which depend on the mutual polarizability of molecules. These forces are usually considered to vary with $1/r^7$.

(5) Repulsive forces due to the mutual impenetrability of completed electronic shells. It is primarily these which determine the collision areas of molecules in the kinetic theory. BORN and MAYER (33) find that the potential energy of these repulsive forces between two completed shells is given by

$$A \exp[(r_1 + r_2 - r)/r_0],$$

where r_1 and r_2 are the effective radii of the two shells and r_0 is a universal constant equal to 0.435 A, while A is another universal constant. This means that this type of repulsive force between two atoms can be expressed as a function of the distances between the *surfaces of the atoms,* this function being the same for nearly all atoms (or molecules) which have completed shells, regardless of their electric charge. From a consideration of several of the other properties of solids and liquids I had previously drawn a similar conclusion (Ref. 20, pp. 529–531), that the repulsive forces should be regarded «as surface forces which should be expressed as functions of the distances between the surfaces of the atoms (fixed by the electron orbits), rather than in terms of the distances between the centers of the atoms». A consideration of VAN DER WAALS' forces showed that for these also the «intensities of the fields around different non-polar molecules are practically identical when regarded as surface forces».

The fact that these repulsive forces, according to BORN and MAYER, decrease to 1/e^th^ value for each increment of 0.435A° in the distance between the atoms, indicates that they have a very small range of action.

(6) *Electron pressures.* The force that counterbalances the COULOMB attraction of the electrons and ions in the alkali metals—and probably in other metals—is that due to the pressure of the FERMI electron gas.

Since all of these forces can be effective at the surface as well as in the interiors of solids and liquids, they must take part in adsorption phenomena. There should thus be various types of adsorption corresponding to the several types of forces which hold the atoms or molecules on the surface. Let us consider some examples:

Caesium on Tungsten. The caesium ions are held by COULOMB attractive forces (here a modified image force) to the underlying metal. The corresponding repulsive forces which hold the ion a definite distance from the surface (and thus determine the dipole moment M) result from the pressure gradient in the FERMI electron gas which extends beyond the lattice of tungsten atoms. The forces between the caesium adatoms ar typical dipole repulsions.

Oxygen on Tungsten or Carbon. The attractive forces are probably typical valence forces. That they are not ordinary Coulomb forces, such as those effective in caesium adsorption, is suggested by a consideration of the relation of the contact potential to the heat of evaporation of the adatoms. A film of caesium which has the maximum effect on the electron emission ($\Theta = 0.67$) has a contact potential of $+3.0$ volts against tungsten, while the heat of evaporation of the adatoms corresponds to 1.9 electron volts. With an oxygen film produced when a tungsten filament at 1,600° is in contact with oxygen at low pressure, the contact potential against tungsten at 1,600° is -1.6 volts, but the heat of evaporation is about 7 volts.

The adsorption of oxygen, hydrogen and carbon monoxide on platinum (36) affords other examples of adsorption dependent on primary valence forces.

Oil Films on Water. In these cases the attractive forces that cause the active heads to spread over the surface are principally dipole forces between the heads and the water molecules with some contribution from van der Waals' forces. Above the heads there is a hydrocarbon phase in which van der Waals' forces and the repulsive forces between completed shells predominate.

Non-Polar Gases on Glass. The adsorption of such gases as nitrogen, argon, etc. on glass or mica at low temperatures is determined by typical van der Waals' forces (24).

Activated Adsorption.

Because of the various types of adsorption that exist, a single gas may be adsorbed by a given surface in several different ways. At sufficiently low temperatures van der Waals' forces alone would be sufficient to cause adsorption (van der Waals' adsorption). At higher temperatures molecules on the surface may undergo chemical change and thus be held by valence forces. The heat of adsorption is then far greater than corresponds to the van der Waals' adsorption. The only reason that such adsorption does not occur at low temperatures is that the reaction velocity of the chemical change may be too low. Since there is an activation energy associated with each such reaction, H. S. Taylor (34) has proposed the term *activated adsorption* for the adsorption which involves such chemical changes.

In some cases, such as the adsorption of caesium atoms on tungsten, the adsorption involves only the transfer of one electron and can thus occur at very low temperatures so that activation is not required, and only one type of adsorption is observed.

The distinction between van der Waals' adsorption and activated adsorption was pointed out by the writer (Ref. 24 pp. 1399–1400) in 1918 and illustrated by the adsorption of carbon monoxide and of oxygen on platinum. At the temperature of liquid air and with a clean platinum surface in contact with carbon monoxide at a pressure of 16 baryes, the surface concentration σ of the adsorbed carbon monoxide was 3.9×10^{14} molecules cm^{-2}, but, as the temperature of the platinum gradually rose to 20°C, σ *decreased* to 1.4×10^{14} and then *increased* again to 3.9×10^{14} and remained nearly constant until 200° C had been reached. When oxygen was brought into contact with platinum at liquid air temperature, 1.5×10^{14} molecules cm^{-2} were adsorbed immediately. On raising the temperature to 20°C, σ increased very slowly (in 18 hours) to 3.0×10^{14}. At 360°C σ rose to 4.8×10^{14}. It was concluded «that at liquid air temperature platinum adsorbs carbon monoxide in much the same way that glass does, that is, by secondary valence forces. With a moderate rise in temperature this gas is released, but in the neighborhood of room temperature the reaction velocity becomes sufficient for the platinum to react (primary valence) with the carbon monoxide to form a much more stable adsorbed film.»

In a discussion of the mechanism of the dissociation of hydrogen on tungsten filaments in 1916 the writer considered (7) the possibility that the adsorbed hydrogen exists on the surface in two forms and that the velocity of interaction between these forms may determine the rate of production of atomic hydrogen. The mathematical formulation which was given is applicable to many cases of activated adsorption.

Within recent years H. S. TAYLOR (34) and his co-workers have discovered many cases of activated adsorption and have demonstrated their importance in an understanding of contact catalysis. The velocity of the activation reaction, which is often low even at a temperature of several hundred degrees, has been measured and the activation energy calculated. Other investigators have sought to explain these slow surface reactions by assuming solution of the adsorbed gas in the underlying substance or slow penetration into cracks or capillary spaces.

That this cannot be a general explanation is proved by some experiments (35) that DR. BLODGETT and I have made on the thermal accommodation coefficient of hydrogen in contact with tungsten. At temperatures from 200°K to 600°K a stable adsorbed film of hydrogen on tungsten is formed which gives an accommodation coefficient α of about 0.22. As the temperature is raised, this film goes over slowly into a much more stable film which is characterized by a value of $\alpha = 0.14$. The reaction velocity is such that the formation of the stable film requires several minutes at 600°K and a small fraction of a second at 900°, indicating an activation energy of the order of at least 20 Kg calories per molecule. Since the accommodation coefficient is a purely surface property, these experiments prove that these two forms of hydrogen film are both monatomic films which probably represent two kinds of chemical binding by valence forces. At temperatures below liquid air temperature a clean tungsten surface would undoubtedly show also VAN DER WAALS' adsorption of hydrogen. This would thus be a third kind of adsorbed film of hydrogen on tungsten.

Catalytic Action of Surfaces. A monatomic film of oxygen on tungsten at 1,500° acts as a catalytic poison for nearly all the reactions which would otherwise occur in contact with the tungsten surface (15). Thus the dissociation of hydrogen into atoms at 1,500°K is stopped by a trace of oxygen, as is also the decomposition of ammonia, methane or cyanogen. The effect of the oxygen is to cover the surface so that the other gas cannot make contact with the tungsten surface.

Similarly hydrogen and carbon monoxide act as catalytic poisons on platinum surfaces (36). The rate at which carbon monoxide and oxygen combine in contact with platinum is proportional to the pressure of oxygen and inversely proportional to the pressure of the monoxide. The reaction velocity depends on that fraction of the platinum surface which is *not covered* by adsorbed molecules of carbon monoxide. The oxygen molecules that can become adsorbed in these vacant spots and so be adsorbed on the platinum surface can thus react with adjacent adsorbed molecules of carbon monoxide.

In numerous cases investigated, the action of a surface in catalyzing a gas reaction involves just such interaction between molecules adsorbed in adjacent elementary spaces on the surface. On this basis it is possible to develop (7) (13) (36) a «law of mass action» for the velocity of surface reactions by which the observed reaction velocities can be explained quantitatively. It has been pointed out (15) that reactions of this sort are extremely sensitive to the actual distances between the atoms in the surface of the catalyst. Thus with many surfaces there is only a relatively small fraction of the surface on which the reaction can occur with extreme rapidity, while over the larger part of the surface it takes place at a negligible rate. A quantum theory explanation of the importance of the spacing of the atoms in the catalyst has recently been given by SHERMAN and EYRING (37).

The presence of a second layer of adsorbed atoms or molecules, although this second layer may cover only a minute fraction of the surface, is often of great importance in the mechanism of gas reactions brought about by a surface catalyst.

Thus in the oxidation of heated tungsten filaments in oxygen at low pressures by which WO_3 is formed, the oxygen molecules incident on a surface already nearly completely covered by a monatomic film of oxygen atoms, condense and momentarily exist in a second adsorbed layer (Ref. 29, p. 473). Although the rate of evaporation from this second layer is so high that the surface concentration is very low, the adsorbed atoms or molecules in this layer move freely over the surface and thus fill up the holes in the first layer, formed when WO_3 molecules evaporate, far faster than would otherwise be possible. These atoms in the second layer can also interact with those in the first layer and with the underlying tungsten to form the molecules of WO_3 which escape from the surface.

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Chapter Five

THE CONSTITUTION OF LIQUIDS WITH ESPECIAL REFERENCE TO SURFACE TENSION PHENOMENA

THE EPOCH-MAKING WORK of LAUE and BRAGG has given us a clear insight into the structure of crystalline bodies. In the case of inorganic crystalline substances, it has been found that the atoms are arranged according to definite lattices so that certain groups of atoms are repeated in a regular manner. In this arrangement, however, there is nothing to indicate where one group ends and the next begins. Thus, in a crystal of common salt, the chlorine and sodium atoms alternate in regular order, but are not grouped together into pairs. Any division of the crystal into molecules is thus purely arbitrary. We must therefore conclude that solid bodies are not built up of molecules, but of atoms arranged in definite ways; or rather, we should regard a crystal as a single large molecule.

From this viewpoint the forces holding solid bodies together (cohesion, etc.) are chemical forces, and phenomena such as evaporation are strictly chemical phenomena. So far, in the study of crystal structure, only inorganic bodies have been investigated. It is certain that in solid organic bodies the atoms are arranged in groups which are usually identical with the molecules found when the substances exist as vapors. We may call these *group molecules*. There are good reasons for believing that in crystals of an organic substance these group molecules are held together by chemical forces (secondary valence) to form single large molecules.

A similar theory is now proposed for the structure of liquids. Each atom in a liquid is regarded as being chemically combined with all adjacent atoms. This chemical union may in general be of two kinds, characterized by *primary* and *secondary* valences. The atoms held together by primary valence usually constitute *group molecules,* in which the atoms are more or less rigidly attached to each other in definite arrangements. The secondary valence serves to hold the group molecules together. In very many cases (such as most inorganic liquids) the group molecules are very much simpler than the usual "chemical molecules" and may often be entirely absent. Thus, in such substances as water, concentrated sulphuric acid or in molten salts or metals, there are probably no group molecules at all; the atoms being held together by secondary valences.

A drop of liquid is thus regarded as a single large molecule. In fact, the whole earth, including the oceans (but excluding the atmosphere) may be looked upon as a single molecule.

The most essential difference between liquids and solids is the mobility of the former. The chemist is already familiar with a mobility between different parts of a molecule and has given the name tautomerism to this phenomenon. The mobility of liquids is therefore a result of tautomeric re-arrangements of the atoms.

Evaporation, condensation, freezing, melting, solution, adsorption, and surface tension, and even viscosity, are thus chemical phenomena, and chemical knowledge already available may be directly applied in their study.

This theory has been applied with marked success in the study of the adsorption of gases by solids. Adsorbed gases are regarded as being chemically combined (either primary or secondary valence) with the *atoms* forming the surface of the solid. The adsorbed film thus usually consists of a *single* layer of atoms or group molecules, which forms a continuation of the structure of the solid. The effect of such films on the catalytic activity of surfaces (as, for example, platinum) depends entirely upon the nature and the arrangement of the atoms forming the actual surface of the solid.

In a similar way a theory of surface tension is now proposed in which the structure of the *surface layer of atoms* is regarded as the principal factor in determining the surface tension (or rather surface energy) of liquids. This theory is supported in the most remarkable way by all available published data on the surface tension of organic liquids.

According to this theory, the group molecules of organic liquids arrange themselves in the surface layer in such a way that their active portions are drawn inwards, leaving the least active portion of the molecule to form the surface layer. By "active portion" of a molecule is meant a portion which is characterized by a strong stray field (residual valence). Chemical action may be assumed to be due to the presence of electromagnetic fields surrounding atoms. Surface tension (or surface energy) is thus a measure of the potential energy of the electromagnetic stray field which extends out from the surface layer of atoms. The molecules in the surface layer of the liquid arrange themselves so that this stray field is a minimum.

The surface energy of a liquid is thus not a property of the group molecules, but depends only on the *least active portions of the molecules* and on the manner in which these are able to arrange themselves in the surface layer.

In liquid hydrocarbons of the paraffin series, the molecules arrange themselves so that the methyl groups (CH_3) at the ends of the hydrocarbon chains form the surface layer. The surface layer is thus the same, no matter how long the hydrocarbon chain may be. As a matter of fact, the surface energy of all these many different substances from hexaine to molten paraffin, have substantially the same surface energy—namely, 46 to 48 ergs per square centimeter, although the molecular weights differ very greatly.

If, now, we consider the alcohols such as CH_3OH, C_2H_5OH, etc., we find that their *surface energies* are *practically identical with those of the hydrocarbons.* The reason for this is that the surface layer in both cases consists of CH_3 groups.

With such substances as CH_3NO_2, CH_3I, we find that the surface energy is much greater than that of the hydrocarbons. This is due to the fact that the volume of the I or the NO_2 is so great that the surface cannot be completely covered by the CH_3 radicals. The forcing apart of these groups increases the surface energy.

Particularly interesting relations are found with benzol derivatives.

In benzol itself, the group molecules arrange themselves so that the benzol rings lie flat on the surface, since the flat sides of these rings are the less active portions of the molecules. The surface energy of benzol is about 65 ergs per square centimeter.

If, now, an active group, such as OH, is substituted for one of the hydrogens in the benzol (forming phenol or carbolic acid), this group is drawn into the body of the liquid, *tilting the benzol ring up on edge* and raising the surface energy to about 75 ergs per square centimeter, which corresponds to the activity of the perimeter of the benzol ring. Thus *any active group* strong enough to tilt the ring up on edge raises the surface energy to about 75. Two active groups side by side (ortho position) have no greater effect than one. But two active groups opposite one another (para position) cannot both go wholly below the surface, so that the surface energy then becomes abnormally large (about 85 in case of para nitrophenol). The substitution of methyl or ethyl groups in the benzol ring lowers the surface energy except where an active group in an adjacent position draws these groups below the surface.

Some of the best evidence in support of the new theory is derived from experiments on thin films of oil on water or mercury. Oleic acid on water forms a film one molecule deep, in which the hydrocarbon chains stand vertically on the water surface with the COOH groups in contact with the water.

Acetic acid is readily soluble in water because the COOH group has a strong secondary valence by which it combines with water. Oleic acid is not soluble because the affinity of the hydrocarbon chains for water is less than their affinity for each other. When oleic acid is placed on water the acid spreads upon the water because by so doing the *COOH can dissolve in the water* without separating the hydrocarbon chains from each other.

When the surface on which the acid spreads is sufficiently large, the double bond in the hydrocarbon chain is also drawn down on to the water surface, so that the area occupied is much greater than in the case of the saturated fatty acids.

Oils which do not contain active groups, as for example pure paraffin oil, do not spread upon the surface of water.

The measurement of the area of water or mercury which can be completely covered by a given amount of a substance affords an accurate method of determining the shapes of group molecules. Thus it is found that the molecules of stearic acid on a surface of water have a length of about 23×10^{-8} cm. and cover an area of 24×10^{-16} sq. cm. These measurements prove that the molecules are not spherical but are much elongated.

This theory also affords an explanation of the mechanism by which colloids are formed. If a film of closely packed oleic acid molecules covers the surface of water to which sodium hydroxide has been added, OH groups are adsorbed by the COOH radicals, causing an expansion of the lower side of the film without a corresponding expansion of the upper side. This results in the bulging of the film downwards in spots so that it finally detaches itself in the form of particles, the outer surfaces of which consist of COOH groups together with the adsorbed OH, while the interior consists of the long hydrocarbon chains.

The size of the colloidal particles is determined by the difference in size between the two ends of the molecules just as the size of an arch is dependent upon the relative sizes of the two ends of the stones of which the arch is constructed.

In the final publication of this paper the bearing of the shapes of molecules on the formation of colloids will be discussed in detail.

Chapter Six

THE DISTRIBUTION AND ORIENTATION OF MOLECULES

When thermal equilibrium prevails the distribution of molecules between two regions in which the potential energies of the molecules are different is given in general by the Boltzmann equation

$$\frac{n_1}{n_2} = e^{\frac{\lambda}{kt}} \tag{1}$$

Here n_{I} and n_2 are the numbers of molecules per unit volume in Regions I and II and λ is the potential energy which must be expended to move a molecule from Region I to Region II, while T is the absolute temperature and k is the Boltzmann constant[1] 1.372×10^{-16} erg per degree. This equation is closely related to the well known Nernst equation for the electromotive force of a concentration cell.

Equation (1) cannot usually be directly applied to the distribution of molecules between separate phases. For example, if we consider the equilibrium between a liquid and its vapor and let n_2 be the concentration in the vapor and n_1 that in the liquid phase we find that (1) must be replaced by

$$\frac{n_1}{n_2} = Ae^{\frac{\lambda}{kt}} \tag{2}$$

The factor A corresponds to the integration constant of the Clapeyron equation for vapor pressures, and its theoretical value must be determined in accordance with the third law of thermodynamics.

A generalized form of the Boltzmann equation has been much used in recent years:

$$\frac{n_1}{n_2} = \frac{p_1}{p_2} e^{\frac{\lambda}{kt}} \tag{3}$$

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[1] The Boltzmann constant is merely the gas constant R expressed per molecule instead of per gram molecule.

Here p_1 and p_2 are defined as the *a priori probabilities* of the molecules in the two regions or two states under consideration. These probabilities are frequently dependent upon geometrical factors, but often involve a knowledge of the quantum phenomena accompanying the change in state. Fortunately the factors p_1 and p_2 vary little if any with temperature and, in the case of related phenomena, the values of p_1/p_2 are often nearly alike, or at any rate their variations produce an effect which is usually small compared to that caused by the exponential factor. Thus the generalized Boltzmann equation becomes of great practical value even when we do not possess sufficient theoretical knowledge to determine the value of the probability coefficients.

The ratio of the concentrations n_1/n_2 is also equal to the ratio P_1/P_2 of the actual probabilities per unit volume for the existence of molecules in the two states, so that

$$\frac{P_1}{P_2} = \frac{p_1}{p_2} e^{\frac{\lambda}{kt}} \tag{4}$$

This equation may be applied for example to study the probability of any particular orientation of a molecule in a liquid, with respect to neighboring molecules or to deal with the orientation of molecules in adsorbed films at interfaces between phases. Equation (3) on the other hand may be used in studying the distribution of molecules between phases and interfaces and also in considering the segregation of certain molecules in the neighborhood of others, due to the local fields of force. Debye and Hückel (*Phys. Zeitschr. 24,* 185, 305 (1923)) for example have recently used the Boltzmann equation to determine the segregation of negative ions around positive ions (and vice versa) and have thus evolved a new theory of electrolytic solutions.

Before we can use Equations (3) and (4) in the way suggested, it is necessary to have definite knowledge of the energy change λ involved in the change of state.

In the case of the molecules of organic substances of non-polar type the so-called physical properties are usually roughly additive. For example, the addition of each CH_2 to a hydrocarbon chain in most compounds containing such chains increases the volume, raises the boiling point, and alters the solubilities in approximately the same way. It is reasonable to assume, therefore, that the field of force about any particular group or radical in a large organic molecule is characteristic of that group and, as a first approximation, is independent of the nature of the rest of the molecule. For convenience we shall refer to this as the *principle of independent surface action.*

It will be readily recognized that this principle lies at the foundation of the theory proposed by the writer in 1916, according to which the surface tension of pure liquids and the properties of adsorbed films at interfaces depend largely upon the orientation of the molecules in the interfaces.

Thus the surface energy[2] γ of all the normal saturated aliphatic alcohols is the same as that of the saturated hydrocarbon hexane, namely 50 ergs per cm.[2] The actual surface energy is that of a hydrocarbon surface in both cases. The alcohol molecules should not be regarded as being packed side by side and arranged with the axes of the hydrocarbon part of the molecule perpendicular to the surface, for there is no force which would compel them to be so arranged. The alcohol molecules which are temporarily in the surface will be free to respond to thermal agitation exactly as if they were in the interior of the liquid, with the single exception that the hydroxyl group cannot itself (for any appreciable fraction of the time) form part of the actual free surface of the liquid. The interaction between the hydroxyl groups of different molecules in the surface is thereby not appreciably altered by the fact that these molecules are forming part of the surface.

The fact of most interest at present is that the hydroxyl group, even in such a small molecule as that of methanol, does not materially alter the surface energy of the CH_3 group which is able to form the actual surface of the liquid by the orientation of the molecule.

The reason that the hydroxyl group avoids the surface must be sought in the energy of the field surrounding this part of the molecule. But by ordinary surface tension and interfacial surface tension measurements we have knowledge of the forces by which hydroxyl groups and hydrocarbon surfaces interact. Let us see whether from such knowledge we cannot determine the energy involved in the orientation of an alcohol molecule and then find from the Boltzmann equation whether this energy is sufficient to cause the orientation indicated by the experiments.

For this purpose let us consider a molecule of methanol. From the density, molecular weight and Avogadro number we find that the volume[3] per molcule is 67.A^3. Assuming close-packed spheres this gives a molecular surface of 65.A^2 and a diameter of 4.56 A. These figures would not be materially altered if we should assume any other reasonable shape for the molecule. We may take half the surface to consist of the hydroxyl group while the CH_3 radical occupies the other half, these areas being each 32.5 A^2.

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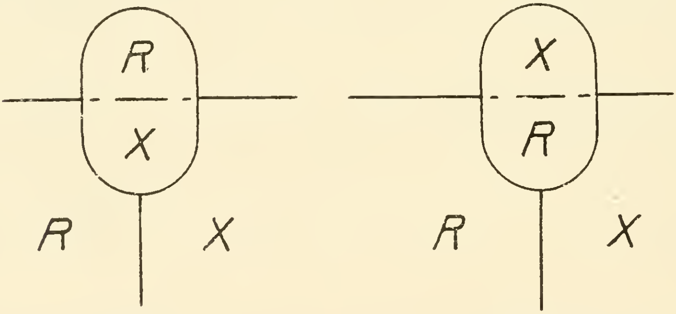
[2] The total surface energy γ is related to the free surface energy γ_f by the equation $\gamma = \gamma_f - T\frac{d\gamma_f}{dT}$. The total energy γ is nearly independent of temperature. From the linear decrease of γ_f with increasing temperature it is probable that the variation of γ_f is a direct result of the thermal agitation of the molecules rather than being due to any change in the structure of the surface. The total energy γ is therefore the quantity which will indicate most clearly any orientation of molecules in the surface.

[3] We shall express the dimensions of molecules in terms of the Ångstrom unit 10^{-8} cm. Areas will be expressed in A^2 (10^{-16} cm^2) and volumes in A^3 (10^{-24} cm^3).

Imagine a molecule of methanol half immersed in a liquid consisting of other methanol molecules as illustrated diagrammatically in Fig. 1. We use R to denote a hydrocarbon radical and X to denote an active group such as hydroxyl. Let us for the present disregard the structure of the liquid and the orientation of the neighboring molecules and consider roughly that half the liquid in contact with the given molecule consists of CH_3 while the other half is OH, as suggested in the diagram. Let us now calculate the surface energy corresponding to the two orientations indicated. If S is the surface of the molecule, γ_R the surface energy of CH_3 and γ_{RX} the interfacial energy between CH_3 and OH radicals then the total surface energy of the molecule in position a is $\frac{1}{2} S\gamma_R + \frac{1}{4} S\gamma_{RX}$ while in position b it is $\frac{1}{2} S\gamma_X + S\gamma_{RX}$. Thus the difference in energy between the two positions which is available for causing the orientation is

$$\lambda = \tfrac{1}{2} S \, (\gamma_X - \gamma_R) \tag{5}$$



Position *a*. Position *b*.

Fig. 1.—Two conceivable orientations of a molecule in the surface of Methanol.

Measurements of the surface energy of hydrocarbons give $\gamma_R = 50$ ergs per cm.^{2} The surface energy of water at 20° is 117, but since the water molecules are decidedly polar they will undoubtedly be oriented in the surface so that this value represents the energy of the least active part of the molecule. We shall see from data on the heat of evaporation of water and alcohol that a more reasonable value for γ_X is 190 ergs per cm^2. Placing $S = 65.A^2$ in Equation (5) we find $\lambda = 22. \times 10^{-14}$ or 46×10^{-14} erg according as we take 117 or 190 as the value of γ_X.

The degree of orientation of the molecules can now be calculated from the Boltzmann equation (4). The probability coefficients p_1 and p_2 may be taken equal since the geometrical probabilities of the two orientations are the same. Putting $T = 293°$ we find $kT = 4.0 \times 10^{-14}$ erg. Thus the exponent is 5.5 or 11.5 according to the two values of $\gamma^{=}$. The corresponding probability ratios P_2/P_1 are 300 and 100000 respectively.

Thus with the lower value of γ^{x} the probability of the orientation a in Fig. 1 is 300 times greater than that of b while with the higher and more reasonable value of γ^{x} the ratio is 100000 to 1.

A more complete justification of the use of the principle of independent surface action is being published elsewhere.[4] A brief summary of the principal results will be given here and then further applications will be made, chiefly dealing with adsorbed films at interfaces.

Evaporation of Pure Substances. Consider a molecule AC (Fig. 2) whose surface S is composite and let a represent the fraction of its surface which is of one kind A (say a hydrocarbon chain) while c is the fraction of the surface which is of the second kind C (say one or more hydroxyl groups). Then

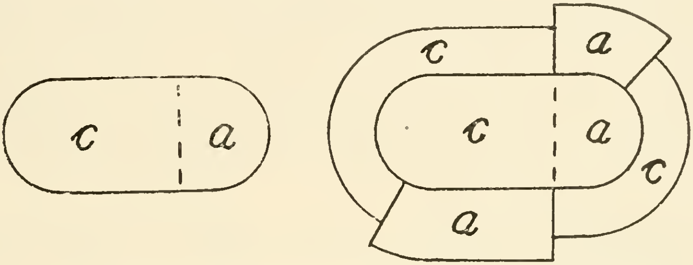


FIG. 2.—Diagram of a molecule AC and of the same molecule in liquid AC.

$$a + c = 1 \tag{6}$$

If we are dealing with a pure liquid each molecule is surrounded by others of the same kind. As a first approximation let us assume that the molecules around a given molecule are neither orientated nor segregated but are arranged in a purely random manner as if no surface energies, λ, were acting. We shall consider later by means of the Boltzmann principle what errors are made by this simplifying assumption.

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[4] A general discussion of the mechanism and the nature of the forces at the surfaces of molecules and applications of the independent surface action to orientation will be published in the book on Colloid Chemistry being edited by Jerome Alexander. A paper giving a detailed mathematical treatment of vapor pressures of liquids and their binary mixtures and of the mutual solubilities of liquids, together with a comparison with available experiment data, is being submitted to the *Journal of Physical Chemistry* for publication.

In Fig. 2 the molecule AC is shown first by itself and secondly, surrounded by others in such a way that the relative areas of the two kinds of surface in contact with each part of the given molecule are in the ratio of a to c.

The area of that part of the molecule which has an A-surface is Sa and of this the fraction c is in contact with the C-surface of surrounding molecules. The corresponding surface energy is $Sac\gamma_{ac}$. Where the A-surface of one molecule is in contact with the A-surface of another there is of course no surface energy.

Similarly the area of contact of the C-surface of the given molecule with the A-surfaces of neighboring molecules is Sca and the corresponding energy is $Sac\gamma_{ac}$. Thus the total surface energy of a given molecule in contact with others is $2Sac\gamma_{ac}$.

Let us now remove the molecule AC to a vapor phase so that it is not in contact with others. Then at the surface of the molecule there is the energy $S(a\gamma_a + c\gamma_c)$ and there is an equal surface energy at the surface of the cavity in the liquid. This latter disappears when the cavity is allowed to collapse but at the same time the new energy $Sac\gamma_{ac}$ appears because of the new interfacial contacts. This energy $Sac\gamma_{ac}$ is half as great as the original energy of the molecule in the liquid, the factor ½ being due to the fact it takes *two* opposing surfaces to make an interface. Thus when the surface S collapses the total interfacial area formed (counting surfaces AA and CC) is only $\frac{1}{2}S$.

The increase in surface energy involved in transferring a molecule from the liquid to the vapor phase is thus

$$\lambda = S\ (a\gamma_a - ac\gamma_{ac} + c\gamma_c) \qquad (7)$$

However if the molecule is a large one it may be so flexible that surface forces tend to make it assume a spherical form when it is in the vapor phase although it may be chain-like in the liquid phase. Also, active groups such as hydroxyl will tend to be drawn into the interior of a large molecule of vapor, just as they are drawn below the surface of the liquid phase. We may neglect the change in S in passing from the liquid to the vapor phase, but may profitably consider that the surface fractions a and c are different in the two cases.

If a_vS and c_vS are the areas of A-surface and C-surface in the molecule of vapor, then $(a\text{-}a_v)S$ is the A-surface which becomes buried within the molecule of vapor. Thus we find that the energy for the transfer of a molecule from the liquid to the vapor is

$$\lambda = S\ [a_v\gamma_a + (a - a_v - ac)\ \gamma_{ac} + c_v\gamma_c] \qquad (8)$$

An analysis of the available data on the heats of evaporation and boiling points of hydrocarbons and alcohols shows that the variation of λ with chemical composition and structure is in excellent agreement with this equation, even in the case of mono-, di- and tribasic alcohols and the compounds having branching chains.

The surface energies γ which give best agreement with these data are

$$\begin{array}{lll} \gamma_R = & 32.7 & \text{for } CH_3 \text{ groups} \\ \gamma_R = & 38.2 & \text{for } CH_2 \quad \text{``} \\ \gamma_X = & 190. & \text{for OH} \quad \text{``} \\ \gamma_{RX} = & 34 & \text{for the interfacial energy of} \\ & & \quad \text{OH against R (hydrocarbon)} \end{array} \qquad (9)$$

The results show unmistakably the tendency for the larger hydrocarbon molecules of vapor to become spherical and for the hydroxyl group to become partly submerged under hydrocarbon groups in the vapor molecule especially when the hydrocarbon chain is long enough for its end to reach back to the hydroxyl group without too sharp curvature. In molecules containing more than one hydroxyl there is a particularly strong tendency for the hydroxyls to come into contact with each other. The surface energies involved in these changes in configuration are sufficient, according to the Boltzmann equation, to overcome the effects of thermal agitation and probably of the constraints due to imperfect flexibility of the molecules.

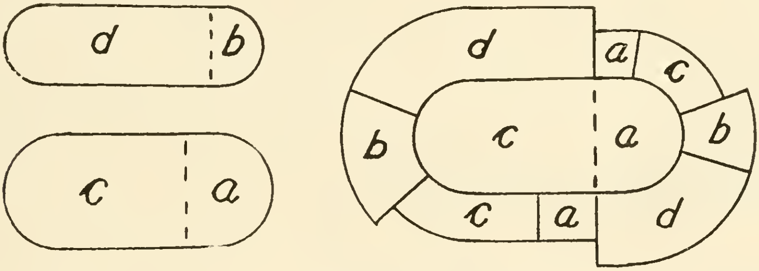

Fig. 3.—Diagram of molecules A and B and of a molecule A in a mixture of A and B.

It is believed that more accurate measurements of vapor pressures of a variety of organic compounds can lead to the development of very definite knowledge of the configurations of their molecules in the vapor phase.

Vapor Pressures of Binary Mixtures. Let us now calculate the energy λ needed to transfer one molecule in a binary mixture to another mixture of the same components having different concentrations. Let us designate the two types of molecules corresponding to the two components by A and B as indicated in Fig. 3. Each molecule is assumed to have a composite surface. The fraction a of the surface of the molecule A is an A-surface, while the fraction c is a C-surface. Similarly b and d are the fractions of the surface of the B molecule which are occupied by B- and D-surfaces respectively, so that

$$a + c = 1 \text{ and } b + d = 1 \tag{10}$$

Let us now consider a binary mixture in which the mol-fraction of A-molecules is A and the mol-fraction of B-molecules is B. The right-hand section of Fig. 3 represents an A-molecule in such a binary mixture. We assume as before that there is neither orientation nor segregation of the molecules which surround a given molecule. Then the relative probabilities that any point on one molecule shall be in contact with an A-molecule or with a B-molecule is proportional to the *total surface areas* of the two kinds of molecules in the mixture. It is thus useful to express the concentrations of the two components A and B in terms of their *surface fractions* which may be defined by the equations

$$\alpha = \frac{S_A A}{S_A A + S_B B} \quad \text{and} \quad \beta = \frac{S_B B}{S_A A + S_B B} \tag{11}$$

where S_A and S_B are the surface areas of the A- and B-molecules respectively. The fractions α and β as well as A and B are related:

$$A + B = 1 \quad \text{and} \quad \alpha + \beta = 1 \tag{12}$$

The surface energy of the A-molecule in the liquid is now found by adding together the energies of each of the five interfaces: AB, AC, AD, BC, and CD. Consider for example the interface AD. The area of the A surface of the A-molecule is aS_A. Of this surface, the fraction β is in contact with B-molecules and of this area of contact the fraction d is a contact with the D-surface. The corresponding surface energy is thus $S_A a\beta d\gamma_{ad}$. For all five terms the surface energy λ_1 is

$$\lambda_1 = S[2\alpha ac\gamma_{ac} + \beta(ab\gamma_{ab} + ad\gamma_{ad} + bc\gamma_{bc} + cd\gamma_{cd})] \tag{13}$$

Now let us imagine that the A-molecule is removed to a vapor phase, leaving a cavity in the liquid. The surface energy λ_2 of the molecule in the vapor phase is

$$\lambda_2 = S(a\gamma_a + c\gamma_c) \tag{14}$$

and the surface energy of the cavity is

$$\lambda_3 = S_A[\alpha(a\gamma_a + c\gamma_c) + \beta(b\gamma_b + d\gamma_d)]$$

When the cavity is allowed to collapse the surface energy λ_3 disappears and new interfaces having the energy λ_4 are produced. The value of λ_4 is found by the summation of 12 terms. The surface of the cavity, before collapse, consists of the areas: $S_A a^4$, $S_A \alpha b$, $S_A \beta b$ and $S_A \beta d$ of the four kinds of surfaces A, B, C and D. Considering that each of these surfaces forms contact with the others in proportion to their respective areas and remembering that it takes two faces to make an interface, we find that the energy λ_4 is

$$\lambda_4 = S_A[\alpha^2 ac\gamma_{ac} + \beta^2 bd\gamma_{bd} + \alpha\beta(ab\gamma_{ab} + ad\gamma_{ad} + bc\gamma_{bc} + cd_{(cd})] \quad (15)$$

The energy λ_{AV} that must be expended in transferring an A-molecule from the liquid phase to the vapor is then

$$\lambda_{AV} = \lambda_2 + \lambda_4 - \lambda_1,$$

the energy λ_3 dropping out. Substituting into this the values from Equations (13), (14) and (15) and replacing α by its value 1 − β we thus find

$$\lambda_{AV} = S_A(a\gamma_a - ac\gamma_{ac} + c\gamma_c - \varphi\beta^2) \qquad (16)$$

where φ is independent of the concentrations of the components and is a function of the γ's:

$$\varphi = ab\gamma_{ab} + ad\gamma_{ad} + bc\gamma_{bc} + cd\gamma_{cd} - ac\gamma_{ac} - bd\gamma_{bd} \qquad (17)$$

In the case of the evaporation of a pure liquid A we place $\beta = O$ in (16) and find for the energy of evaporation

$$\lambda'_{AV} = S_A(a\gamma_a - ac\gamma_{ac} + c\gamma_c) \qquad (18)$$

so that Equation (16) simplifies to

$$\lambda_{AV} = \lambda'_{AV} - S_A\varphi\beta^2 \qquad (19)$$

If we have two binary mixtures (1 and 2) having the same components but in different concentrations, the energy required to transfer an A-molecule from 1 to 2 is, according to (19)

$$\lambda_A = S_A\varphi(\beta_2^2 - \beta_1^2) \qquad (20)$$

and in a similar way it may be shown that the energy of transfer of a B molecule from 1 to 2 is

$$\lambda_B = S_B\varphi(\alpha_2^2 - \alpha_1^2) \qquad (21)$$

As the first application of these equations let us make a comparison of the energy λ_A' for the transfer of a molecule A from a pure liquid A to a pure liquid B, with the energy λ_B' for the transfer of a B molecule from B to A. In liquid A, $\alpha = 1$ and $\beta = 0$ while in B, $\alpha = 0$ and $\beta = 1$ and Equations (20) and (21) reduce to

$$\lambda_A' = S_A\varphi \quad \text{and} \quad \lambda_B' = S_B\varphi \qquad (22)$$

The energy of transfer of molecules A and B between two pure liquids A and B is thus proportional to the surface areas of these molecules.

The Boltzmann equation may now be used to calculate the distribution of molecules between the vapor phase and a binary mixture of liquids. If we let p_A be the partial pressure of the A-molecules in the vapor then by the generalized Boltzmann equation (3) we have

$$\frac{p_A}{A} = Ke^{-\frac{\lambda_{AV}}{kT}} \tag{23}$$

where λ_{AV} is given by Equation (19) and K is a constant into which are grouped as factors the *a priori* probabilities and the dimensional factors needed to allow us to express the concentrations in the liquid in terms of the mol-fraction A while that of the vapor phase is expressed as a pressure p. We are hereby making the tacit but reasonable assumption that the probability coefficients are independent of the concentrations of the components. The vapor pressure P_A of the pure liquid A is given by (22) if we place $A = 1$ and $\lambda_{AV} = \lambda_{AV}'$ so that

$$P_A = Ke^{-\frac{\lambda_{AV}'}{kT}} \tag{24}$$

Dividing (23) by (24) and by combining with (19)

$$p_A = P_A A e^{\frac{S_A \varphi}{kT} \beta^2} \tag{25a}$$

and in a similar way the partial pressure of component B is

$$p_B = P_B B e^{\frac{S_B \varphi}{kT} \alpha^2} \tag{25b}$$

These equations for the vapor-pressures of binary mixtures reduce to the well known Raoult's law when $\varphi = 0$, that is, when the energy of mixing is zero.

Comparison with experimental data, particularly with the accurate data of Zawidski (J. v. Zawidski, *Zeit. phys. Chem.* *35*, 129–203 (1900)) shows that even for liquids which depart considerably from Raoult's law these equations, which involve only one adjustable constant φ, usually agree with the data within the experimental error. In the case of mixtures in which S and S differ considerably, the use of these factors and the use of the surface fractions α and β instead of the mol fractions, are found to be thoroughly justified.

The rather meager experimental data available show that in changing from one member of a homologous series of compounds to another, in a given type of mixture, the values of φ change in general in the manner indicated by (17).

Some typical values of φ calculated from published experimental data on vapor pressures of binary mixtures are given in Table I. It is seen that the values of φ are of the order of magnitude of the surface tensions of liquids, but are smaller than these in accord with the fact that in Equation (17) (which gives φ) the coefficients are all less than unity and two of them are negative.

It can be shown from (17) that φ should approach zero if the A molecules and the B molecules become alike in regard to both their values of γ and their surface fractions a and b. We see from Table I that the observed values of φ are very small for mixtures of closely related substances such as ethanol-methanol, benzene-toluene, and methyl acetate-ethyl acetate. The series of benzene mixtures 9 to 15, which are arranged in the order of the φ's, show how φ increases as the substance mixed with the benzene becomes less like it, until with methanol φ becomes 10 ergs per cm.^{2}

TABLE I

"Mixture Energies" φ for Various Binary Mixtures

Mixture	Ref.[5]	Temp. ° C.	φ ergs per cm ^{2}
1. Carbon disulfide–Acetone	Z	35	+ 6.9
2. Water–Pyridine	Z	80	+ 12.9
3. Carbon tetrachloride–Ethyl acetate	Z	50	+ 1.18
4. Ethyl acetate–Ethyl iodide	Z	50	+ 1.90
5. Ethyl iodide–Carbon tetrachloride	Z	50	+ 0.9
6. Hexane–Ethyl iodide	v. H.	60	+ 2.6
7. Acetone–Chloroform	S	50	— 2.9
8. Carbon disulfide–Chloroform	S	50	+ 2.15
9. Benzene–Chloroform	S	40	— 0.4
10. Benzene–Ethyl ether	S	40	— 0.1
11. Benzene–Toluene	S	40	+ 0.50
12. Benzene–Carbon tetrachloride	Z	50	+ 0.57
13. Benzene–Carbon disulphide	S	40	+ 2.1
14. Benzene–Methyl acetate	S	40	+ 2.5
15. Benzene–Methanol	S	40	+ 10.1
16. Methanol–Ethanol	S	40	0.0
17. Methyl acetate–Ethyl acetate	S	40	+ 0.4

In the case of mixture No. 6, hexane-ethyl iodide, there are only two kinds of molecular surface (R and I) and therefore the 6 terms of Equation (17) reduce to one, so that the value of γ (R-I) can be calculated from the observed value of φ. The three binary mixtures Nos. 3, 4 and 5 involve only 3 components. Because of the symmetry of carbon tetrachloride ($a = 1$, $c = 0$) and the fact that ethyl acetate and iodide both contain hydrocarbon (R) surfaces, Equation (17) becomes much simplified. By means of the values of φ for the 3 mixtures Nos. 3, 4 and 5 we obtain 3 equations containing 5 unknown values of γ. From a study of the surface tensions and other properties of alkyl chlorides and iodides we may conclude that chlorine has properties intermediate between alkyl and iodine. Thus it is reasonable to assume that $\gamma(\text{Cl-I}) = \gamma(\text{R-Cl})$. We have seen in (9) that $\gamma(\text{R-OH}) = 34$ and there are several indications that the relation of -COO- to R is not materially different from that of OH to R. Thus we place $\gamma(\text{R-C}) = 34$, using C as an abbreviation of the -COO- group in esters. We then have five equations for our five unknowns and thus find the values given in Table II.

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[5] Data indicated by Z are those of Zawidski (l.c.); S are from rough measurements of the total pressures of binary mixtures, by G. C. Schmidt, *Zeit. phys. Chem.*, *99*, 71 (1921); v.H. is from H. v. Halban, *Zeit. Phys. Chem.*, 84, 129 (1913).

From these values it should be possible to calculate the vapor pressures of any binary mixtures of compounds such as RCl, RI, RCOOR where each R represents any alkyl group. There is also no difficulty in including compounds containing two or more Cl, I or -COO- groups.

It should also be possible from the principles that have been outlined to develop equations for ternary mixtures and for those containing compounds with molecules having three or more kinds of surface. Thus from the values of γ in Table II we should be able to calculate the partial vapor pressures of a ternary mixture consisting of say propyl-di-chlor acetate, ethylene chloride and amyl iodide, from the vapor pressures of the separate components and the ordinary data of molecular volumes.

TABLE II

VALUES OF SURFACE ENERGY γ CALCULATED FROM EXPERIMENTAL DATA ON VAPOR PRESSURES

Surfaces	Symbol	γ ergs per cm^2
1. Hydrocarbon–Iodine	$\gamma(\text{R–I})$	13.7
2. Hydrocarbon–Chlorine	$\gamma(\text{R–Cl})$	4.1
3. Hydrocarbon–COO–	$\gamma(\text{R–C})$	33.7
4. Chlorine–Iodine	$\gamma(\text{Cl–I})$	4.1
5. Chlorine–COO–	$\gamma(\text{Cl–C})$	17.7
6. Iodine–COO–	$\gamma(\text{I–C})$	16.6

Unfortunately there have been very few experimental studies of the vapor pressures of a series of related compounds which can serve at present as a test of this theory.

Measurements are needed of the vapor pressures of binary mixtures of hexane with different simple alkyl compounds such as ethanol, propionic acid, ethyl chloride, etc. From each such mixture studied, a separate value of γ can be obtained and it would then be easy to calculate the vapor pressures of other mixtures of such compounds, and thus check the theory by corresponding experiments.

The boiling points of many binary mixtures of alcohols, bromides, iodides and acetates have been measured by Holley (*Jour. Amer. Chem. Soc., 24,* 448 (1902)) and by Holley and Weaver (*Jour. Amer. Chem. Soc., 27,* 1049 (1905)). For mixtures containing 0.5 mol fraction of each component the total vapor pressure of the mixture was compared with that of the separate pure components and then by a series of trials the partial pressure and φ were calculated by Equations (25).

TABLE III

Observed and Calculated Mixture Energies φ for Binary Mixtures of Alkyl Bromides and Alcohols

Alcohol	Propyl Bromide		Iso (?)–Butyl–Bromide		Amyl Bromide	
	φ_{obs}	φ_{cal}	φ_{obs}	φ_{cal}	φ_{obs}	φ_{cal}
Methanol	8.90	8.76	7.33	8.52	7.30	8.33
Ethanol	6.97	5.82	6.61	5.58	5.90	5.40
Propanol	5.39	4.52	3.24	4.28	—	—
Butanol	3.43	3.76	2.89	3.53	—	—
Pentanol	3.77	3.21	—	—	—	—

Table III gives a summary of the values φ_{obs} which were thus obtained from the experimental data on mixtures of bromides with alcohols. The values marked φ_{cal} have been calculated[6] by Eq. (17) from the following values of γ.

Hydrocarbon-bromine $\gamma(\text{R-Br}) = 10.$ ergs per cm.^{2}
Hydrocarbon-hydroxyl $\gamma(\text{R-OH}) = 33.7$
Bromine-hydroxyl $\gamma(\text{Br-OH}) = 49.6$

The value of $\gamma(\text{R-Br})$ was assumed to be 10 as a reasonable interpolation between $\gamma(\text{R-I}) = 13.7$ and $\gamma(\text{R-Cl}) = 4.1$ as given in Table II. The values of $\gamma(\text{R-OH})$ and $\gamma(\text{Br-OH})$ were then determined by least squares to make the agreement as good as possible between φ_{obs} and φ_{cal} in Table III.

Considering the rather rough nature of these data and the uncertainty in some cases as to whether the normal or iso-compounds were used, the agreement is as good as could be expected. The signs of the differences between φ_{obs} and φ_{cal} seem to be distributed nearly at random.

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[6] The surfaces S of the molecules were calculated from the molecular weights and the densities at room temperature, assuming arbitrarily close packed spheres. The surface fractions a, b, c and d were calculated by taking for the surface of the bromine atom 25.A^2 and for the hydroxyl group 30.A^2.

It is interesting to note that the value of $\gamma(\text{R-OH}) = 33.7$ obtained from these data on the vapor pressures of mixtures of bromides and alcohols agrees with the value 34 given in (9) for γ^{RX} which corresponds to the energy of the same kind of interface, but determined in an entirely different way, viz., from the heats of evaporation of alcohols.

Perhaps the best test of Equation (17) available at present is that based on the published data on the vapor pressures of mixtures of alcohols and water and mixtures of fatty acids and water, although the polar character of these substances undoubtedly causes some mutual orientation and segregation of molecules in these mixtures, so that the assumptions underlying this equation are not completely fulfilled.

Table IV contains the results of calculations based on Wrewsky's data (M. Wrewsky, *Zeit. phys. Chem. 81,* 1 (1913) and *82,* 551 (1914)) on the partial vapor pressures of aqueous mixtures of methyl, ethyl and propyl alcohols at temperatures of 30° and 50°.

TABLE IV

THE MIXTURE ENERGIES φ OF ALCOHOL-WATER MIXTURES

Alcohol	α	φ_{obs}	φ_{cal}
Methanol	0.460	6.1	6.02
Ethanol	0.359	11.5	11.69
Propanol	0.305	15.1	15.0

φ_{cal} is based upon
$\gamma(\text{R–OH}) = 33.7$
$\gamma(\text{R–H}_2\text{O}) = 37.4$ and
$\gamma(\text{OH–H}_2\text{O}) = -12.6$

The value of $\gamma(\text{R-OH})$ was taken to be the same as found from the data of Table III, and the other two γ's were chosen to make φ_{obs} and φ_{cal} agree as well as possible. The fact that the *two* constants could be chosen so as to give such good agreement with the *three* values of φ_{obs} is evidence for the applicability of Equation (17) from which φ_{cal} was derived.

In these calculations the water molecule was assumed to have a single kind of surface. The value $\gamma = 37.4$ is in reasonable agreement with the value 59 obtained by Harkins for the total surface energy of a hexane-water interface by direct measurement.

The *negative* surface energy $\gamma = -12.6$ for the interface between water and the hydroxyl group is not contrary to known facts and is an expression of the very strong effect of this radical in increasing the solubility of organic substances in water.

Table V gives a summary of calculations based upon Konowalow's data (*Ann Phys., 14,* 34 (1881)) on the total vapor pressures of mixtures of water with various fatty acids. The values of γ found from these data are in reasonable agreement with others of similar nature already found. These data are, however, probably only rough. The known existence of double molecules in the vapors of the lower fatty acids should cause deviations from our theory, but the effect is probably not sufficient to prevent the theory from serving as a useful approximation over a wide range of concentrations.

TABLE V

THE MIXTURE ENERGIES φ OF FATTY ACID-WATER MIXTURES

Acid	α	φ_{obs}	φ_{cal}
Formic	0.739	-15.0	-13.6
Acetic	0.549	$+2.5$	$+1.1$
Propionic	0.459	$+8.0$	$+8.5$
Butyric	0.402	$+13.8$	$+13.4$

φ_{cal} is based upon
$\gamma(\text{R-COOH}) = 20.0$
$\gamma(\text{R-H}_2\text{O}) = 51.4$
$\gamma(\text{H}_2\text{O-COOH}) = -31.2$

Mutual Solubilities of Liquids. When two immiscible liquids, A and B, are in equilibrium, each has dissolved some of the other, and the partial vapor pressure p_A from one liquid must be the same as the p_A from the other. Thus, from Equations (25) we obtain the following two equations which express the solubilities of the liquids in one another

$$\frac{A_1}{A_2} = e^{\frac{S_A\varphi}{kT}(\beta_2^2 - \beta_1^2)}$$

and (26)

$$\frac{B_1}{B_2} = e^{\frac{S_B\varphi}{kT}(\alpha_2^2 - \alpha_1^2)}$$

The subscripts 1 and 2 refer to the two phases.

If each liquid is only very slightly soluble in the other, the equations take the simple form

$$A_2 = e^{-\frac{S_A\varphi}{kT}} \quad \text{and} \quad B_1 = e^{-\frac{S_B\varphi}{kT}} \tag{27}$$

If $S_A = S_B$ then $\alpha = A$ and $\beta = B$ and the two Equations (26) can readily be combined to one of the convenient form

$$\frac{1+\Delta}{1-\Delta} = e^{\frac{S\varphi}{kT}} \tag{28}$$

where $\Delta = A_1 - A_2 = B_2 - B_1$.

We then find that $\Delta = 0$ or $A_1 = A_2$ at a critical temperature T_c given by

$$T_c = \frac{S\varphi}{2K} \tag{29}$$

Above this temperature the liquids are miscible in all proportions, so that there is only one phase, while at lower temperatures two phases exist.

The values of φ calculated from these equations come out usually somewhat lower (10 to 30%) than those from vapor pressures and are probably less accurate. Undoubtedly, in mutually saturated liquids, especially near the critical temperature, the conditions are favorable for orientation and segregation of the molecules in the liquids, so that we should not expect our equations for solubilities to hold as well as those for the vapor pressures of mixtures of liquids which mix in all proportions.

Nevertheless, the general agreement between the theory and the experimental data seems very satifactory, especially if we are willing to consider mainly relative rather than the absolute values of φ.

The effects of the relative surface areas of the molecules indicated by Equations (27) seem to be well verified by the experimental data. Thus, in general, for two substances only slightly soluble in one another, the substance having the molecules of the larger surface shows the lower solubility in the other.

TABLE VI

SOLUBILITIES OF FATTY ACIDS IN WATER

n	Acid	Temp.	Observed Solubility Mol Fraction	a	φ_{obs}	φ_{cal}
4	Butyric	$-2°$	0.052	0.402	10.5	13.3
5	Valeric	16°	0.0062	0.357	15.0	17.3
9	Nonylic	25°	1.4×10^{-5}	0.272	26.0	25.0
14	Myristic	20°	ca. 10^{-8}	0.198	33.0	31.9

Even when solubilities are large, nearly to the point of complete mixing, the same rule applies. For example, the critical temperature of butyric acid-water mixtures is $-2.5°$ C. At $-6°$ C. there are two phases. The water phase contains 0.053 mol fraction of butyric acid, but the acid phase contains 0.76 mol fractions of water. The much greater solubility of the water as compared to the acid corresponds to the smaller surface area of the water ($S_B = 37.8\text{A}^2$) as compared to that of the acid ($S = 115\text{A}^2$). In fact the difference in solubility is almost exactly what the theory indicates, for the value of φ calculated by Equations (26) from A_1/A_2, involving the solubility of the acid, is 16.9 ergs per cm.^{2} while B_1/B_2, from the solubility of the water, gives very nearly the same value, viz. $\varphi = 9.7$. These are to be compared with $\varphi = 13.6$ from Table V for butyric acid-water mixtures at higher temperature from vapor pressure data.

From the very rough data available on the solubilities of higher fatty acids we obtain the values given in Table VI.

The 5th column gives the surface fraction a corresponding to the carboxyl group whose actual surface is taken to be 45A^2. The 6th column gives the value of φ_{obs} obtained by Equations (26) from the observed value of the solubility while the 7th column gives φ_{cal} which is calculated by Equation (17) with the same values for the γ's as those already used for the calculations of Table V.

It will be seen that the agreement is reasonable and indicates that the marked decrease in solubility of the fatty acids in water as we pass to the higher fatty acids is fully explained by our theory of independent surface action.

It is important to note that the solubility *of water* in the fatty acids does not continue to decrease without limit as the length of chain increases. As soon as the solubilities have become small Equations (27) are applicable. As the length of chain increases a approaches zero and φ approaches the limiting value 51.4 corresponding to $\gamma(\text{R-H}_2\text{O})$ (see Table V). We see, however, from (27) that S_A, the area of the molecule of acid, continues to increase as the chain lengthens and thus A, the solubility of the acid in water, decreases without limit. On the other hand, S_B, the area of the water molecule, remains constant so that the solubility B, of water in the acid, decreases only because of the increasing φ and thus approaches a limiting value as the chain lengthens.

ORIENTATION OF MOLECULES IN A LIQUID PHASE

Thus far we have considered particularly the distribution of molecules between different phases on the assumption that there is no mutual orientation of the molecules within the phases. Although the agreement of our theory with experiment proves that in the case of many liquids this orienting effect is negligible, it is believed that such orientation (and corresponding segregation) is the main cause of deviations which occur with the more polar substances.

For example, the vapor pressures of mixtures of alcohols with water give values of φ which are nearly constant or independent of the concentration, except that the values obtained from the partial pressures of water over the mixtures containing more than about 0.5 mol fraction of water give values of φ which are much too low. Thus, although the partial vapor pressures of methanol over the whole range agree with the value $\varphi = 6.1$, and the partial pressures of water from solutions containing less than 0.5 mol fraction of water also agree with this value reasonably well, the values of φ for the higher concentrations of water decrease rapidly, so that with a mixture containing 0.8 mol fraction of water $\varphi = -20$. With ethanol and propanol similar effects exist but are much less marked.

In order to form a more concrete conception of the principles which govern the orientation of organic molecules within a liquid, let us consider the following model. The inner circle in Fig. 4 represents a molecule AC, the sector *a* being the A-surface. The annular space between the two circles represents diagrammatically the surfaces of the molecules which surround the given molecule AC. In choosing the symbols *a, b, c, d* to represent the surface fractions we may, without loss of generality, so assign them among the 4 kinds of surface that $b < a < c < d$. When the molecule AC is oriented as shown, with the whole of the B-surface in contact with A-surface, all of the C-surface will be in contact with D-surface and the surface fraction of A-surface in contact with D is $a - b$. Thus the total surface energy is

$$\lambda_1 = S[b\gamma_{ab} + (a - b)\gamma_{ad} + c\gamma_{cd}] \tag{30}$$

Let the molecule AC now be turned so that the A-surface does not come into contact with B but only touches D. Then the total surface energy is

$$\lambda_2 = S[a\gamma_{ad} + b\gamma_{bc} + (c - b)\gamma_{cd}] \tag{31}$$

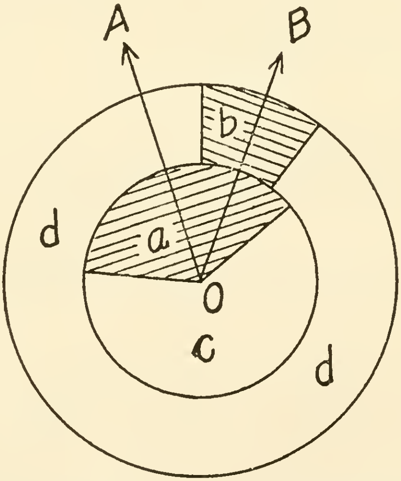

FIG. 4.—Diagram illustrating the orientation of a molecule AC in a liquid BD.

These two orientations correspond to the extreme values of the surface energy; when A and B are partly in contact with each other the energy λ has intermediate values. The difference $\lambda_2 - \lambda_1$ which we shall refer to as λ_0 is thus the greatest surface energy which can be effective in causing orientation.

$$\lambda_0 = Sb(\gamma_{ad} + \gamma_{bc} - \gamma_{ab} - \gamma_{cd}) \tag{32}$$

For convenience let us place

$$\gamma_0 = \gamma_{ad} + \gamma_{bc} - \gamma_{ab} - \gamma_{cd} \tag{33}$$

so that

$$\lambda_0 = Sb\gamma_0 \tag{34}$$

The unique occurrence of b in these expressions is due to the fact that b is the smallest of the surface fractions a, b, c and d because of the convention of nomenclature that we have adopted.

We may represent any given orientation of a molecule AC in Fig. 4 by a given position of the vector OA with respect to the vector OB. If AC passes through all possible orientations we may imagine OA as passing over all points on a spherical surface. We may represent all orientations within any given solid angle by the ratio of the spherical surface described by the vector OA, to the total spherical surface, this ratio being called a surface fraction.

The difficulties in the complete solution of the 3-dimensional problem of orientation are considerable and we may therefore content ourselves with treating it as if it were a 2-dimensional problem. We shall assume therefore that the molecule AC in Fig. 4 has cylindrical symmetry and can rotate only about its axis.

There are three cases to consider.

I. The molecule is so oriented that the whole of the B-surface is in contact with A. Surface fraction $(a - b)$.

II. The whole of the B-surface is in contact with C. Surface fraction $(c - b)$.

III. Part of B is in contact with A while the remainder is in contact with B. Surface fraction $2b$.

We may let P be the probability per unit surface fraction that the molecule may be oriented as in Case I. The total probability that a molecule shall be so oriented is thus $P(a - b)$.

The probability that the molecule shall be oriented in Case II may be found by the Boltzmann Equation (4) and is

$$P(c-b)e^{\sigma}$$

where

$$\sigma=\frac{\lambda_0}{kT}=\frac{Sb\gamma_0}{kT} \tag{35}$$

Within the region corresponding to Case III the surface energy varies linearly between two limits, so that we find the total probability that the molecule shall come under Case III is

$$P\int_0^{2b} e^{\frac{\sigma x}{2b}}\,dx$$

Now since the molecule must be oriented in one of these 3 ways the sum of these 3 probabilities is unity

$$1=P[(a-b)+(c-b)e^{\sigma}+\int_0^{2b} e^{\frac{\sigma x}{2b}}\,dx \tag{36}$$

If we assume that λ_0 is small enough, σ will be small compared to unity so that we may expand e^{σ} into a series taking only the terms involving the first order in σ. The foregoing equation thus becomes

$$1=P(1+c\sigma) \tag{37}$$

which gives us the values of P.

We may now determine the average surface energy obtained from all possible orientations by weighting each orientation in proportion to its probability. We thus find, taking only terms up to the first order in σ

$$\lambda=\lambda_1+P\lambda[c+\sigma(c-\tfrac{1}{3}b)] \tag{38}$$

Since $b<a<c$ we may neglect $1/3b$ in comparison with c. Substituting the value of P from (37) we can reduce Equation (38) to

$$\lambda=\lambda_1+\lambda_0c(1+\sigma a) \tag{39}$$

and by (34) we obtain

$$\lambda=\lambda_1+Sbc(1+\sigma a)\gamma_0 \tag{40}$$

This equation allows us to determine theoretically whether the molecules in a given mixture are oriented to an appreciable extent, and if so, we may then estimate the magnitude of the effect produced. Let us consider the following cases:—

1. $\sigma = -\infty$. Equation (40) is inapplicable, but by the method used in the derivation of Equation (36) we see that all the molecules will be oriented as in Case I and the surface energy is thus equal to λ_1 as given in Equation (30). Practically speaking we have this case, if σ is negative and $-\sigma$ is large compared to unity, which occurs if $-Sb\gamma_0$ is large compared to kT.

2. $\sigma = +\infty$. This case is approached if γ_0 is positive and $Sb\gamma_0$ is large compared to kT. The molecules are nearly all oriented as in Case II so that the energy is λ_2 as given by (31) or

$$\lambda_2 = \lambda_1 + \lambda_0 \tag{41}$$

3. $\sigma = 0$. This corresponds to an entire absence of orienting force. The molecules are thus arranged wholly at random. Equation (40) gives

$$\lambda_R = \lambda_1 + Sbc\gamma_0 \tag{42}$$

Substituting in this the value of λ_1 by (30) and the value of γ_0 from (33) we find

$$\lambda_R = S(ab\gamma_{ab} + ad\gamma_{ad} + bc\gamma_{bc} + cd\gamma_{cd}) \tag{43}$$

Equation (13) was derived as an expression for the energy of a molecule AC surrounded by molecules AC and BD without orientation or segregation. For the case in hand, where AC is surrounded only by molecules BD, we place $\alpha = 0$, $\beta = 1$ and find that Equation (13) then reduces to Equation (43) as of course it should.

4. σ *small compared to unity.* This is the case when $Sb\gamma_0$ is small compared to kT. Equation (40) then applies. Let us consider how the energy λ then differs from λ_R the energy corresponding to random orientation. From (40) and (42) we get

$$\lambda - \lambda_R = Sabc\sigma\gamma_0 = \frac{S^2ab^2c\gamma_0^2}{kT} \tag{44}$$

This equation enables us to estimate what error we have made in the early part of this paper by assuming a random distribution of molecules in liquids, as for example, in the derivation of Equations (11) to (17).

As a specific example, let us apply Equation (44) to calculate the effect of orientation of ethanol molecules in various mixtures of ethanol with hexane. We have already found that the interfacial energy γ(R-OH) is 34 ergs per cm.^{2} The surface S_A of ethanol molecules may be taken to be 83.5A^2 while that of hexane molecules is 136A^2. The surface $S_A a$ of the hydroxyl group in the ethanol molecule is 30A^2. With these data we find from Equation (17) $\varphi = 4.39$ ergs per cm. for ethanol-hexane mixtures and from this, by Equations (25) we can calculate the partial vapor pressures of these mixtures. We now wish to determine what corrections should be applied to these results to take into account the orienting effect of the ethanol molecules on each other.

We see from Equation (20) that the energy needed to transfer an ethanol molecule from pure ethanol to a mixture is

$$\lambda_A = S_A \varphi \beta^2$$

where β is the surface fraction of hexane in the mixture. This expression was substituted in the exponent of the Boltzmann equation to obtain Equation (25a) which would give the uncorrected vapor pressure of ethanol. To get the corrected vapor pressures we should add to γ_A, before making this substitution, the correction given by Equation (44). We place in Equation (33) $\gamma_{ad} = \gamma_{bc} = 34$ and $\gamma_{ab} = \gamma_{cd} = 0$ and obtain $\gamma_0 = 68$. From the value of S_A and S_B we find $a = 0.359$ and $c = 0.641$. Thus Equation (44) becomes

$$\lambda - \lambda_R = 2.72 \times 10^{-14} b^2 \text{ erg} \tag{45}$$

The choice of the value b is a matter which requires careful analysis. Suppose the mixture is nearly pure hexane containing only a small amount of ethanol. Most of the ethanol molecules will be surrounded only by hexane molecules so that for these molecules $b = 0$. There will be some ethanol molecules, however, whose surface will be in contact with hydroxyl groups of adjacent molecules. For these the value of b will be determined by the area of contact between two hydroxyl groups.

When molecules are arranged like close packed spheres each is in contact with 12 others, so that the area of contact is $S/12$. We may suppose that about 3 of these 12 regions of contact, for the hydroxyl radical in an alcohol, are occupied by the union with the alkyl group. Thus the surface of 30 A^2, which we have taken as the effective surface of the hydroxyl, represents 9 possible regions of contact, each contact having an area of 3.3 A^2. Allowing for a probable deformation we may thus take the area of contact between adjacent hydroxyl groups to be roughly 3.5A^2, or 4.2 per cent of the whole surface of an ethanol molecule. Since the surface fraction of the hydroxyl in *pure* ethanol is 0.359 and the surface fraction of each contact is 0.042, we see that there should be on the average 0.359/0.042 = 8.5 hydroxyl groups in contact with each ethanol molecule. In a mixture of ethanol with hexane in which the mol fraction of ethanol is $A = 0.117$ (*i.e.* 1/8.5) each ethanol molecule will be in contact, on the average, with one hydroxyl group. For such a mixture we may therefore put $b = 0.042$. Equation (45) then gives

$$\lambda - \lambda_R = 0.0048 \times 10^{-14} \text{ erg} \tag{46}$$

With lower concentrations of ethanol the fraction of the ethanol molecules which are in contact with hydroxyl groups is proportional to the concentration. Thus for these low concentrations we obtain for the average energy correction

$$\lambda - \lambda_R = 0.041 \times 10^{-14} A \text{ erg} \tag{47}$$

which gives the same value as (46) when $A = 0.117$.

For higher concentrations of ethanol than $A = 0.117$ there will usually be more than one contact with hydroxyl. However, these will not in general be adjacent but will be distributed nearly according to the laws of chance. If they were distributed absolutely *uniformly* over the surface of the ethanol molecules there would be no tendency to orient these molecules.

According to the probability laws therefore the effective surface area, $S_A b$, of contact with the hydroxyl groups should be proportional to the square root of the number of contacts. Since, by (45) the energy varies as b^2 it is thus directly proportional to the number of contacts or is proportional to the concentration A. Therefore Equation (47) gives the value of $\lambda - \lambda_R$ for concentrations above $A = 0.117$, as well as for concentrations below this value.

In general we may thus assume that $\lambda - \lambda_R$ is proportional to A as in Equation (47) and may place

$$\lambda - \lambda_R = MA \tag{48}$$

where M is the proportionality factor.

Going back to the derivation of Equations (25) from (19), (22) and (23) we may now correct the value of λ_{AV} in (19) by means of (48) obtaining

$$\lambda_{AV} = \lambda_{AV}' - S_A \varphi \beta^2 + MA \tag{49}$$

Instead of (24) we then find

$$P_A = K e^{\frac{\lambda_{AV}' + M}{kT}} \tag{50}$$

and (25) is replaced by

$$p_A = P_A A e^{\frac{S_A \varphi \beta^2 + MB}{kT}} \tag{51}$$

In the example we are considering (ethanol-hexane) the term MB is $0.041 \times 10^{-14} B$ while $S_A \varphi \beta^2$ is $3.66 \times 10^{-14} \beta^2$ so the effect of orientation of molecules is practically negligible.

In the foregoing analysis we have considered the orientation of a given ethanol molecule by surrounding molecules which are oriented in random directions. Actually these molecules will tend to be oriented by the given molecule and this in turn would increase the orienting effect on the original molecule. It is probable that value of $\lambda - \lambda_R$ given by (45) or (48) should be approximately doubled to take into account this mutual orientation.

In any case we may conclude that with mixtures of many common organic compounds there will be no appreciable orienting effect and that we are therefore justified in assuming a random orientation as a first approximation. The magnitude of the orienting effect is sufficient, however, for it to become of considerable importance as-a cause of deviations in the case of polar substances, and particularly of those whose molecules act as dipoles.

ORIENTATION OF MOLECULES IN INTERFACES

The example of the orientation of alcohol molecules in a free surface which was considered in the introduction has served to show how the principle of independent surface action may be applied in such cases.

When a sufficiently small amount of a substance such as palmitic acid is placed upon a clean surface of water in a tray the surface tension of the water is not appreciably lowered. But if the free surface of the water is decreased, by sliding a strip of paper over its surface, the surface tension begins to decrease quite suddenly when the free surface becomes about 20 A^2 per molecule of palmitic acid. By raising the temperature of the water or by introducing traces of acid into the water, the point at which the surface tension begins to decrease may occur at an area of 30 to 50 A^2. Such films may be called expanded films.

In 1917 in a discussion[7] of the arrangement of molecules in adsorbed films on the surfaces of fatty acid solutions it was concluded that in dilute solutions "the hydrocarbon chain lies spread out flat on the surface of the water, but as the concentration of the solution increases, the molecules become more closely packed and when the surface becomes saturated, the molecules are all arranged with their hydrocarbon chains placed vertically." The transition between the two states was assumed to take place in the manner that was suggested (on page 1865) for the expanded film of oleic acid, viz., in the expanded film "the molecules are partly reclining on the surface, while in the second case (compressed film) they are packed tightly side by side and are more or less erect upon the surface."

The area covered by a vertically placed palmitic acid molecule is about 20 A^2 while the same molecule lying flat on the surface should cover an area of about 108 A^2. Clearly then the expanded films occupying an area of at most 50 A^2 must consist of molecules which are only slightly inclined from the vertical. As a matter of fact there is no reason at all why the flexible hydrocarbon chains should orient themselves at any particular angle. They will be quite free to respond to thermal agitation and arrange themselves nearly in the same random manner as in a liquid hydrocarbon, the only restriction upon their motion being imposed by the condition that the *lower end* of each molecule must remain in contact with the underlying water. We can thus readily see why the expanded films are *always liquid* while the contracted or fully compressed films of vertically oriented molecules are frequently *solid*. Taking the volume of the hydrocarbon chain in the palmitic acid molecule as 450 A^3 we see that the thickness of the hydrocarbon layer (in A units) will be $450 \div a$ where a is the area of the film per molecule (in A^2 units). Thus when $a = 20$ A^2 the thickness is 22.5 A while for an expanded film for which $a = 33$ A^2 the thickness is 13.6 A.

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[7] Langmuir, *Jour. Amer. Chem. Soc., 39,* 1848 (1917).

Consider an expanded film as covering a definite area of a water surface. If additional palmitic acid molecules are introduced into the film there is no change in the area of the free hydrocarbon surface. The energy of transfer of a molecule from any given location to an expanded film is thus the same as the energy of transfer of the molecule to an interface between hydrocarbon and water. The total surface energy λ for a molecule of palmitic acid at the edge of a condensed film is -17 while for a molecule in an expanded film λ is -37. This would indicate that the expanded film should form in preference to the condensed film. However the difference of 20 in the values of λ is not greater than the probable error so that the sign of the difference is somewhat uncertain. In considering the stability of expanded films we must take into account the applied compressive force and the effect of the forces acting between the heads of the molecules which are located in the interface between the hydrocarbon film and the water. To understand these relationships better let us analyze the problem as follows.

Let n molecules of a substance (which spreads on water) be present per unit area as an expanded film on the surface of the water. The flexible hydrocarbon tails of the molecules are subject to little or no constraint except that due to the fact that they are attached to the heads which must remain in contact with the water.

The expanded film may thus be looked upon as a layer of hydrocarbon liquid having at its upper surface a surface energy γ and having adsorbed in its interface with the water n active groups, or heads per unit area. Consider now that by means of a *two-dimensional piston* (for example a paper strip on the surface) the expanded film is allowed to cover only a part of the surface of the water. The spreading force F (in dynes per cm.) exerted by the film is measured by the mechanical force applied to the piston. On one side of the piston is a surface of water which exerts a force γ_W tending to cause the film to expand and on the other side is the expanded film whose *upper surface* exerts a force γ_R while the *lower surface* exerts a force which we may represent by γ_L. Thus for equilibrium we have

$$\gamma_W - F = \gamma_R + \gamma_L$$

If the molecules in the film did not have any active groups, the surface tension γ_L would be equal to the normal interfacial energy γ_{RW}. But the *active groups in the interface* because of their thermal agitation will tend to act like a two-dimensional gas. When these active groups or heads are far enough apart they will exert a force F_L following the gas law

$$F_L = nkT \text{ or } F_L a = kT \tag{52}$$

where a is the area per molecule.

When the molecules are packed as closely as in the ordinary expanded film, we should, by the analogy with the b term in the van der Waals equation, write

$$F_L\,(a - a_0) = kT \tag{53}$$

where a_0 is the area per molecule for a highly compressed film.

Furthermore the analogy with the equation of state for gases would suggest that when the film is compressed sufficiently, attractive forces between the active groups would come into play and that these might be largely responsible for the small spreading forces observed with some contracted films. In any case, however, we may place

$$\gamma_L = \gamma_{RW} - F_L \tag{54}$$

and thus from Equation (51) we get

$$F = \gamma_W - \gamma_R - \gamma_{RW} + F_L \tag{55}$$

For very low compressive forces we may neglect the attractive forces between the heads and thus by combining Equations (55) and (53) we get

$$(F - F_0)(a - a_0) = kT \tag{56}$$

as our equation of state for expanded films. Here F_0 is used as an abbreviation for the three γ terms in (55) so that

$$F_0 = \gamma_W - \gamma_R - \gamma_{RW} \tag{57}$$

Thus we see that we should not expect the simple gas law of Equation (52) to hold for expanded films, but such a law should hold only after constants F_0 and a_0 have been subtracted from the observed values of F and a.

Examination of the experimental data on expanded films in my 1917 paper, and in Adam's papers [8] show that the agreement with Equation (56) is very satisfactory. For large compressive forces deviations occur which are of the kind that are to be expected as a result of attractive forces between the heads of the molecules. For example, Adam's curve (in this 3rd paper) for a film of myristic acid on water at 32.5°C. gives the equation

$$(F + 13)\ (a - 18) = kT$$

The value of a_0 is thus 18.A^2 while F_0 has the value -13 dynes per cm.

Let us compare this value of F_0 with that calculated by Equation (57). For water at 32.5° the free energy (surface tension) γ_W is 71.0 dynes per cm. The interfacial free surface energy γ_{RW} of octane is 50.4. Since the temperature coefficient is very low the total interfacial energy is about the same as the free energy. Our theory of the structure of the interface leads to the conclusion that the *total energy* is independent of the length of the hydrocarbon chain and since in this case the free energy and total energies are nearly the same the free energy will also be independent of the chain length. Thus for tetradecane (the hydrocarbon corresponding to myristic acid) we may put $\gamma_{RW} = 50.4$.

The free surface energy of octane at 32.5° is 20.4 and the total energy is 48.4. For tetradecane the theory indicates that the total energy will also be 48.4. The free surface energy is a linear function of temperature and becomes zero at the critical temperature. Taking the critical temperature of tetradecane as 680° K we can thus estimate that the free surface energy at 32.5° C. should be 26.7.

These values for the γ's give $F_0 = +0.2$ for octane and $F_0 = -6.2$ dynes per cm. for hexadecane. This latter value does not differ greatly from that calculated from Adam's data on the myristic acid films ($F_0 = -13$). The difference is not greater than should be expected because of the uncertain part played by thermal agitation in the spreading of surfaces.

According to Equation (56) with negative values of F_0 the expanded film should not expand indefinitely even if the compressive force F is made negligibly small. Placing $F = 0$ we see that the maximum area covered per molecule will be

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[8] N. K. Adam, *Proc. Royal Soc. A,* 99, 336 (1921); 101, 452, 516 (1922); 103, 676, 686 (1923); 106, 694 (1924); *Jour. Phys. Chem.,* 29, 87 (1925).

$$a_M = a_0 - \frac{kT}{F_0} \tag{58}$$

For the case we have considered where $a_0 = 18$, and $F_0 = -13$, we obtain $a_M = 18 + 32.3 = 50.3$ A^2 as the maximum area for an "expanded film" of myristic acid on water. This equation shows that the maximum area a_M depends principally upon F_0. By Equation 57 we see that F_0 is the difference between two relatively large quantities which are nearly equal. A very small percentage change in γ_R causes a relatively large change in F_0 and therefore in a_M. As a matter of fact Adam finds that a_M varies only moderately for different substances. As the length of the chain increases he finds a slight decrease in a_M and considers this a strong argument against the view that the molecules tend to lie flat if they have sufficient room to do so. We have seen, however, by our comparison of octane with tetradecane that γ_R and therefore $-F_0$ increase with the length of the chain, and therefore, by Equation (58), a_M should actually increase as the chain is made shorter. The changes in a_M observed by Adam may be accounted for by very small percentage changes in γ_R.

This theory of "expanded films" requires that the molecules remain in contact while Adam concluded that in such films the "molecules become separated and move about independently on the surface" and that "there are spaces not covered by molecules." Adam considered that the *molecules* of the film behaved as a two-dimensional gas while we conclude that it is only the heads of the molecules that behave in this way.

The fact that a palmitic acid film shows no measurable tendency to expand beyond a certain definite area is in accord with the following values of λ which have been calculated from the γ's by the principle of independent surface action.

$\lambda_1 = 181 \times 10^{-14}$ erg for a molecule oriented vertically in a water surface with the carboxyl group down and surrounded by water molecules except at its upper end which reaches the free surface.

$\gamma_2 = 64 \times 10^{-14}$ for a molecule lying flat in the surface with the carboxyl group turned downward into the water at one end of the molecule.

$\gamma_3 = 4 \times 10^{-14}$ for a horizontal molecule at the edge of a film of vertically placed close-packed molecules.

$\lambda_4 = -17 \times 10^{-14}$ for a vertically placed molecule at the edge of a film of similar vertical molecules.

The difference between λ_4 and λ_1 or λ_2 is so great that according to the Boltzmann equation no appreciable number of molecules can remain isolated in the surface. The few molecules that do exist as separate molecules, however, must all lie flat in the surface because of the great difference between λ_2 and λ_1.

If we consider lower members of the fatty acid series we find that the difference between λ for the single molecules and for those in clusters becomes much smaller so that separate molecules do exist and therefore the surface tension of water is decreased by even dilute films of these acids in which a, the area per molecule, is very much greater than in expanded films of palmitic acid. The values of λ prove that in such two-dimensional "gaseous" films the molecules lie flat in the surface.

Chapter Seven

ATOMIC HYDROGEN AS AN AID TO INDUSTRIAL RESEARCH

I BELIEVE the primary object of the Perkin Medal is to do honor to the memory of Sir William Perkin, that pioneer who devoted himself to pure scientific research after having led in the industrial applications of research for fifteen years. This object is best attained by encouraging the kind of research that he valued so highly. The medal should thus be regarded, not as a reward for accomplishment nor as a prize to stimulate competition in research, but rather as a means of directing attention to the value of research and to the methods of research that are most productive. Having this in mind, I am going to tell you, although somewhat reluctantly, the history of some of my own work, in so far as it illustrates a method of industrial research that has proved valuable.

TWO TYPES OF INDUSTRIAL RESEARCH

The leaders of industries are frequently conscious of the need of improvement in their processes, and even of the need of new discoveries or inventions which will extend their activities. It is thus logical, and often extremely profitable, to organize research laboratories to solve specific problems. Efficiency requires that the director shall assign to each worker a carefully planned program. Experiments which do not logically fit in with this program are to be discouraged. This type of industrial research, which should often be called engineering rather than research, has frequently been very successful in solving specific problems, but usually along lines already foreseen.

This method, however, has serious limitations. Directors are rare who can foresee the solutions sufficiently well to plan out a good campaign of attack in advance. Then, too, the best type of research man does not like to be told too definitely what must be the objects of his experiments. To him scientific curiosity is usually a greater incentive than the hope of commercially useful results. Fortunately, however, with proper encouragement, this curiosity itself is a guide that may lead to fundamental discoveries, and thus may solve the specific problems in still better ways than could have been reached by a direct attack; or may lead to valuable by-products in the form of new lines of activity for the industrial organization.

Of course, no industrial laboratory should neglect the possibilities of the first and older method of organized industrial research. I wish, however, to dwell upon the merits of the second method in which pure science or scientific curiosity is the guide.

HISTORY OF THE GAS-FILLED LAMP

I first entered the Research Laboratory of the General Electric Company in the summer of 1909, expecting in the fall to return to Stevens Institute, where I had been teaching chemistry. Instead of assigning me to any definite work, Doctor Whitney suggested that I spend several days in the various rooms of the laboratory, becoming familiar with the work that was being done by the different men. He asked me to let him know what I found of most interest as a problem for the summer vacation.

A large part of the laboratory staff was busily engaged in the development of drawn tungsten wire made by the then new Coolidge process. A serious difficulty was being experienced in overcoming the "offsetting" of the filaments, a kind of brittleness which appeared only when the lamps were run on alternating current. Out of a large number of samples of wire, three had accidentally been produced which gave lamps that ran as well with alternating as with direct current, but it was not known just what had made these wires so good. It seemed to me that there was one factor that had not been considered—that is, that the offsetting might possibly be due to impurities in the wire in the form of gases. I therefore suggested to Doctor Whitney that I would like to heat various samples of wire in high vacuum and measure the quantities of gas obtained in each case.

In looking through the laboratory I had been particularly impressed with the remarkably good methods that were used for exhausting lamps. These methods were, I thought, far better than those known to scientific research workers. My desire to become more familiar with these methods was undoubtedly one of the factors that led me to select for my first research an investigation of the gas content of wires.

After starting the measurements that I had planned, I found that the filaments gave off surprisingly large quantities of gas. Within a couple of weeks I realized that something was entirely wrong with my apparatus, because from a small filament in a couple of days I obtained a quantity of gas which had, at atmospheric pressure, a volume 7000 times that of the filament from which it appeared to have come; and even then there was no indication that this gas evolution was going to stop. It is true that in the literature—for example in J. J. Thomson's book on the "Conduction of Electricity through Gases"—one found many statements that metals in vacuum give off gases almost indefinitely, and that it is impossible to free metals from gas by heating. Still I thought that 7000 times its own volume of gas was an entirely unreasonable amount to obtain from a filament. I spent most of the summer in trying to find where this gas came from, and never did investigate the different samples of wire to see how much gas they contained. How much more logical it would have been if I had dropped the work as soon as I found that I would not be able to get useful information on the "offsetting" problem by the method that I had employed.

What I really learned during that summer was that glass surfaces which have not been heated a long time in vacuum slowly give off water vapor, and this reacts with a tungsten filament to produce hydrogen, and also that the vapors of vaseline from a ground-glass joint in the vacuum system give off hydrocarbon vapors, which produce hydrogen and carbon monoxide.

That summer's work was so interesting that I dreaded to return to the comparative monotony of teaching, and gladly accepted Doctor Whitney's offer to continue at work in the laboratory. No definite program of work was laid down. I was given first one assistant and then others to continue experiments in the sources of gas within vacuum apparatus, and a study of the effects produced by the introduction of various gases into tungsten filament lamps. The truth is that I was merely curious about the mysterious phenomena that occur in these lamps. Doctor Whitney had previously found that gases have a habit of disappearing in lamps, and no one knew where they went to, so I wanted to introduce each different kind of gas that I could lay my hands on into a lamp with a tungsten filament and find out definitely what happened to that gas.

It was the universal opinion among the lamp engineers with whom I came in contact that if only a much better vacuum could be produced in a lamp a better lamp would result. Doctor Whitney, particularly, believed that every effort should be made to improve the vacuum, for all laboratory experience seemed to indicate that this was the hopeful line of attack on the problem of a better lamp. However, I really didn't know how to produce a better vacuum, and instead proposed to study the bad effects of gases by putting gases in the lamp. I hoped that in this way I would become so familiar with these effects of gas that I could extrapolate to zero gas pressure, and thus predict, without really trying it, how good the lamp would be if we could produce a perfect vacuum.

This principle of research I have found extremely useful on many occasions. When it is suspected that some useful result is to be obtained by avoiding certain undesired factors, but it is found that these factors are very difficult to avoid, then it is a good plan to increase deliberately each of these factors in turn so as to exaggerate their bad effects, and thus become so familiar with them that one can determine whether it is really worth while avoiding them. For example, if you have in lamps a vacuum as good as you know how to produce, but suspect that the lamps would be better if you had a vacuum, say, 100 times as good, it may be the best policy, instead of attempting to devise methods of improving this vacuum, to spoil the vacuum deliberately in known ways, and you may then find that no improvement in vacuum is needed or, just how much better the vacuum needs to be.

During these first few years, while I was thus having such a good time satisfying my curiosity and publishing scientific papers on chemical reactions at low pressures, I frequently wondered whether it was fair that I should spend my whole time in an industrial organization on such purely scientific work, for I confess I didn't see what applications could be made of it, nor did I even have any applications in mind. Several times I talked the matter over with Doctor Whitney, saying that I could not tell where this work was going to lead us. He replied that it was not necessary, as far as he was concerned, that it should lead anywhere. He would like to see me continue working along any fundamental lines that would give us more information in regard to the phenomena taking place in incandescent lamps, and that I should feel myself perfectly free to go ahead on any such lines that seemed of interest to me. For nearly three years I worked in this way with several assistants before any real application was made of any of my work. In adopting this broad-minded attitude Doctor Whitney showed himself to be a real pioneer in the new type of modern industrial research.

For my study of the effect of gases, I had to devise new types of vacuum apparatus. I needed particularly to be able to analyze the small quantities of gas that existed in the tungsten lamp. With some of this special apparatus I was able to make a practically complete quantitative analysis of an amount of gas which would occupy about 1 cu. mm. at atmospheric pressure. In this sample of gas we could determine the percentages of oxygen, hydrogen, nitrogen, carbon dioxide, carbon monoxide, and the inert gases.

In regard to the fate of the different gases which I introduced into the lamp bulb, I found that no two gases acted alike. Oxygen attacked the filament and formed tungstic oxide, WO_3. That seemed simple enough, but the kinetics of the reaction presented many features of considerable scientific interest.

In studying the effect of hydrogen very peculiar phenomena were observed. A limited amount of hydrogen disappeared and became adsorbed on the bulb, where it remained in a chemically active form, which was capable of reacting with oxygen at room temperature even long after the tungsten filament had been allowed to cool. This suggested hydrogen atoms and seemed to confirm some conclusions that I had already drawn from observations on the heat losses from tungsten filaments in hydrogen at atmospheric pressure. In making squirted tungsten filaments, and sometimes in cleaning the drawn wire, filaments were heated in this manner in hydrogen. Because tungsten filaments melt at a temperature more than 1500° higher than platinum, it had seemed to me that tungsten furnishes a tool of particular value for the scientific study of phenomena in gases at high temperatures. From my work on lamps I knew approximately the relation between the resistance of tungsten wire and its temperature, and could thus use a tungsten wire as a kind of resistance thermometer. By connecting a voltmeter and an ammeter to the tungsten filament which was being heated in hydrogen, I could determine the temperature from the resistance and also find the heat loss from the filament in watts. I wanted to see if anything abnormal happened when the temperature was raised to the extremes which were only possible with tungsten.

The results greatly interested me, for they showed that the energy loss through the gas, which increased in proportion to the square of the temperature up to about 1800° K., increased at a much higher rate above that, until at the highest temperatures the energy varied in proportion to about the fifth power of the temperature. This result could be explained if the hydrogen at high temperatures were dissociated into atoms. The diffusion of the hydrogen atoms from the filament, and their recombination at a distance from it, would cause an enormous increase in heat conduction. After publishing these preliminary results, I was naturally much interested in getting other information in regard to the properties of these hydrogen atoms. A large number of experiments, extending over several years, were thus made in this study of atomic hydrogen. Nearly all of these experiments would have seemed quite useless, or even foolish, to a man who was making a direct and logical attack on the problem of improving tungsten lamps.

When nitrogen at low pressure was introduced into a bulb containing a tungsten filament at extremely high temperatures, such as 2800° K., the nitrogen disappeared at a rate which was independent of its pressure; in other words, here was a case of a reaction of zeroth order. This suggested that the reaction velocity was limited by the rate at which the tungsten evaporated from the filament. To check this hypothesis the rate of loss of weight of filaments at various temperatures was measured in good vacuum. This rate varied with the temperature in accordance with known thermodynamic laws, and since the rate per unit area was independent of the size of the filament, it was concluded that the loss of weight was really due to evaporation and not to chemical action of residual gases or to electric currents that passed from the filament to the surrounding space.

A comparison of the rate of disappearance of nitrogen with the loss of weight in the filament showed that one molecule of nitrogen disappeared for every atom of tungsten that evaporated. A brown compound, WN_2, was formed which deposited on the bulb and decomposed when water vapor was introduced, forming ammonia gas.

From time to time the question kept arising—how good would a lamp be if it had a perfect vacuum? And now, from studies of the character I have described, I began to have an answer. Hydrogen, oxygen, nitrogen, carbon monoxide, and in fact every gas that I introduced, with the exception of water vapor, did not produce blackening of the lamp bulb. The serious blackening that occurred with only small amounts of water vapor depended upon a cyclic reaction in which atomic hydrogen played an essential part. The water-vapor molecules coming in contact with the hot filament produce a volatile oxide of tungsten, and the hydrogen is liberated in atomic form. The volatile oxide deposits on the bulb where it is reduced to the metallic state by the atomic hydrogen, while the water vapor produced returns to the filament and causes the action to be repeated indefinitely. Thus, a minute quantity of water vapor may cause a relatively enormous amount of tungsten to be carried to the bulb.

The question then arose whether the traces of water vapor, which might still exist in a well-exhausted lamp, were responsible for the blackening which limited the life or the efficiency of many of these lamps. We made some tests in which well-made lamps were kept completely immersed in liquid air during their life, so that there could be no possibility of water vapor coming in contact with the filament. The rate of blackening, however, was exactly the same as if no liquid air had been used.

Having thus proved that the blackening of a well-made lamp was due solely to evaporation, I could conclude with certainty that the life of the lamp would not be appreciably improved even if we could produce a perfect vacuum.

Early in 1911 William Stanley, one of the pioneers in the electrical industry, felt that our company should do more fundamental work in connection with heating devices. Since I had become interested in the theory of heat losses from filaments in gases, I was glad to work along these lines, so I undertook to direct a small laboratory at Pittsfield, Mass., at which I spent about two days a week. Besides studying the heat losses from plane surfaces at various temperatures, I measured the heat losses from wires of various sizes in air at different temperatures, working at first with platinum wires, and was able to develop a theory of the heat losses which enabled me to calculate the loss from a wire of any size at any temperature in any gas, assuming, however, that the gas did not dissociate at high temperatures.

Having now a definite theoretical basis on which to calculate the normal loss by convection, I was able to prove that the abnormal rate of heat loss previously observed with tungsten filaments at high temperatures in hydrogen was due to actual dissociation; in fact I was thus able to calculate the heat of dissociation and the degree of dissociation at different temperatures.

However, to make sure of these conclusions I wished to make measurements of the heat losses in gases which could not possibly dissociate, and therefore undertook experiments with heated tungsten wires in mercury vapor at atmospheric pressure. A little later I experimented with nitrogen to see if this gas dissociated at high temperatures, but found that it did not do so. In both of these gases the filaments could be maintained at temperatures close to the melting point for a far longer time than if heated in vacuum at the same temperature. Thus the rate of evaporation was greatly decreased by the gas, many of the evaporating tungsten atoms being brought back to the filament after striking the gas molecules.

By this time I was familiar with all the harmful effects which gas can produce in contact with filaments and knew under what conditions these bad effects could be avoided. In particular, I realized the importance of avoiding even almost infinitesimal traces of water vapor. Thus, when I found a marked effect of mercury vapor and nitrogen in reducing the rate of evaporation, it occurred to me that it might be possible to operate a tungsten filament in gas at atmospheric pressure and obtain a long useful life. Of course, it would be necessary to raise the temperature far above that at which the filament could be operated in vacuum in order to compensate for the serious loss in efficiency due to convection by the improved efficiency resulting from the rise in filament temperature. Whether or not the increased rate of evaporation, due to this increase in temperature, would more than offset the decrease in the rate due to the gas was a matter that could only be tested by experiment.

In connection with my studies of the heat losses from filaments of various diameters at incandescent temperatures, I had found that the heat loss increased only very slowly with the diameter, so that the loss per unit area from a small filament was enormously greater than from a large filament. Calculations showed that it was hopeless to get practical lamps with filaments in nitrogen, if these filaments were of very small diameter. For example, a filament 1 mil in diameter, which corresponds to an ordinary 25-watt lamp, if run in nitrogen at atmospheric pressure would consume 4.8 watts per candle at a temperature of 2400° K., which would give 1 watt per candle with a filament in vacuum. This great loss in efficiency is due to the cooling effect of gas. To bring back the efficiency of the gas-filled lamp to that of the vacuum lamp, it would be necessary to raise the temperature from 2400° to 3000° K., which would have caused a 2000-fold increase in the rate of evaporation, and such an increase could certainly not be compensated for by the effect of the gas in retarding the evaporation.

With filaments of much larger diameter, however, the effect of the gas in decreasing the efficiency was not nearly so marked. We therefore constructed lamps having filaments of large diameter in the form of a single loop and filled these lamps with nitrogen at atmospheric pressure. We ran these lamps with a filament temperature so high that, in spite of the gas, the efficiency corresponded to about 0.8 watt per candle instead of the usual 1 watt per candle at which we tested our vacuum lamps. We were disappointed to find that these lamps blackened much more rapidly than vacuum lamps of similar efficiency so that the total useful life of the lamp was short.

This result, which is what most lamp engineers would have expected, seemed to indicate that the rise in temperature necessary to offset the heat losses by the gas increased the evaporation by more than the amount of the reduction in evaporation due to the gas. If I had not previously become so familiar with the behavior of various gases, this discouraging result might easily have stopped further experimenting in this direction. However, I noticed that the bulb had blackened during the short life of the lamp, whereas from my knowledge of the interaction of tungsten and nitrogen I had expected a deposit of a clear brown color. I felt that the black deposit, therefore, could mean only one thing, water vapor, notwithstanding the fact that to avoid this water vapor we had taken precautions which were greater, I believe, than had ever been used before for the preparation of moisture-free gases and glass surfaces. We were thus led to take still greater precautions and use still larger bulbs, so that the glass surfaces could not become overheated by the convection currents in the gas that rose from the filament. We were then soon able to make lamps having a life of over 1000 hours with an efficiency about 30 to 40 per cent better than could have been obtained with filaments in vacuum.

As I look back upon these experiments I think that we were very fortunate at that time in not having had at our disposal a supply of argon gas. From theoretical reasons I had concluded that argon should be better than nitrogen, and if I had had argon I should probably have tried it first. If these lamps had blackened because of traces of water vapor, I would naturally have attributed this to the increase in evaporation caused by the high temperature, and would have had no reason for suspecting that water vapor was the cause of the trouble, for, of course, in argon a brown deposit would not be expected in any case.

The lamps that we were able to make in this way, with an improved efficiency, were limited to those which took a current of 5 amperes or more, so that the method was not applicable for 110-volt lamps with less than 500 watts. Some time later, however, it occurred to me that the benefits derived from the large diameter of the filament could be obtained with one of smaller diameter by coiling the filament in the form of a helix, bringing the turns of the helix very close together. In this way, and by the use of improved tungsten filaments that do not sag so readily at high temperatures, and by using argon instead of nitrogen, it has gradually been possible to construct gas-filled lamps which are better than vacuum lamps down to about 40 or 50 watts. These smaller lamps, although not much better in efficiency than the vacuum lamp, have the advantage of giving a much whiter light. In the case of the larger lamps, the use of the gas filling, together with the special construction of the lamp, more than doubles the efficiency.

The invention of the gas-filled lamp is thus nearly a direct result of experiments made for the purpose of studying atomic hydrogen. I had no other object in view when I first heated tungsten filaments in gases at atmospheric pressure. Even at the time that I made these experiments at higher pressures, they would have seemed to me useless if my prime object had been to improve the tungsten lamp.

I hope I have made clear the important role that properly encouraged scientific curiosity can have in industrial research. The illustration that I have given is not at all exceptional. I could have given any one of several others equally well. Many industrial laboratories have followed Doctor Whitney's lead, in devoting a fairly large fraction of their activities to these rather purely scientific researches. Certain men, at least, are not expected to be responsible for practical applications, but are freely allowed to make fundamental scientific investigations. The type of man who does this work best can usually only be attracted to those industrial laboratories that have adopted this policy.

However, I do not believe that this second method of research is growing in popularity solely because it is found to be profitable. I feel rather that most of our leaders in industrial research are eager to adopt this method, in so far as economic factors may permit, because they realize the debt that modern industry owes to the pure science of the past and because the modern conception of service and the growing *esprit de corps* of American industry help make them glad of any opportunity to contribute to scientific knowledge. I know personally that such motives as these have guided Doctor Whitney in the leadership he has taken.

I believe in the near future there will be a much increased demand for men with scientific training who are capable of doing more independent thinking.

BETTER EDUCATION NEEDED

Our schools and universities devote so much effort in imparting information to students that they almost neglect the far more important function of teaching the student how to get for himself what knowledge of any subject he may need. Even in grammar school children are crammed with more information on arbitrarily selected subjects than even the average well-educated adult can retain. Of course students should be taught the fundamental principles of mathematics, and of various sciences as well as of other subjects, but much of the knowledge of data upon which these principles depend and necessary information should be obtained by the efforts of the student through experimentation and individual reading.

In looking back on my own school and college days, it seems to me that the things of most value were learned spontaneously through interest aroused by a good teacher, while the required work was usually comparatively uninteresting. The university student should have leisure for some independent work and opportunities for continuing his interest in hobbies of various kinds which he should have had long before he entered college. I realize that it is difficult so to arouse the student's interest that he will spend the added leisure in these ways rather than in spending still more on the bleachers, cheering the football team in their practice games, but a well-planned effort is worth while.

The importance of arousing even a young boy's interest in independent work can hardly be overemphasized. My real interest in science was derived from my brother Arthur, who encouraged me to have a workshop at the age of nine, and later a laboratory when I was only twelve.

I can illustrate my father's influence in stimulating independence by the following incident: When I was twelve I climbed one or two Swiss mountains of moderate height with my older brother, Arthur. Soon after Arthur had to go to Heidelberg to arrange for his studies, leaving me with my mother and younger brother at a hotel in the Rhone Valley. I had become so enthusiastic over mountain climbing that I wished to climb everything in sight, but the dangers were such that my mother did not dare let me go alone. When my father arrived for a week-end visit from Paris, he consented to allow me to climb alone any mountain I liked if I would promise to do it in accord with the following three rules: (1) I must stay on a distinct trail; (2) I must use the same trail going and returning; (3) I must make certain of returning at six o'clock by allowing as much time for descending as for ascending. Before these rules went into effect, however, I had to prove that I could and would make such sketches, maps, and notes of the trails used for the ascent that I could always return by the same route. I thus climbed several mountains about 7000 feet high, often requiring several days of repeated effort before I could discover a route that led to the top. Perhaps it is this experience which makes me even today always wish to find my own way rather than be told.

Until I was fourteen I always hated school and did poorly at it. At a small boarding school in the suburbs of Paris, however, being an American and having a friend who was influential with the head of the school, I was freed from much of the absurdly rigorous discipline to which the French boys were subjected. Thus, I could spend time alone in the school laboratory and was encouraged by one of the teachers to learn to use logarithms and solve problems in trigonometry, subjects not required by the curriculum.

I have been fortunate in having many wonderful teachers. Three of them have been recipients of this Perkin Medal. Whitaker and Chandler were my teachers at Columbia and Whitney during the last eighteen years. Prof. R. S. Woodward, at Columbia, in connection with his courses in mechanics, was extremely stimulating and encouraged me to choose and solve my own problems for class work instead of those required in the regular course.

I should like to see spontaneous work of this kind take a much more prominent part in our educational system—at least for students who have more than average ability.

THE VALUE OF HOBBIES

Very great benefit may be derived from hobbies. Probably each person should have several of them. Recently I met a small boy, only six years old, who had an overpowering, wide-eyed enthusiasm for collecting insects. He weighed each one of them within a milligram, and then, after desiccating them thoroughly over calcium chloride, weighed them again. Many elaborate notes and even correspondence resulted. I am afraid our universities, with their dormitories and other standardizations, tend to discourage such wholesome individual activities.

After talking of hobbies, I cannot resist the temptation to tell something about my own. Perhaps my most deeply rooted hobby is to understand the mechanism of simple and familiar natural phenomena. I will give only two illustrations, but these, I hope, will show how easy it is to find around us simple phenomena that are not well understood.

Every chemist knows that after he stirs a liquid in a beaker having a precipitate in the bottom, the precipitate collects near the center. Probably few know why this is so. It is not due to the slower velocity of rotation near the center, nor to the slower motion with respect to the glass. This is proved by the fact that if you put the beaker, with the precipitate in suspension in the liquid, upon a rotating table, the precipitate will collect in a ring as far from the center as possible, although the relative angular motion of the beaker and its contents is the same as before. A little study proves that the phenomena are due to unbalanced centrifugal forces. For example, when the liquid is stirred to set it in rotation, centrifugal force produces a greater hydrostatic pressure near the walls of the beaker. But the liquid very close to the bottom surface of the beaker, because of friction, cannot rotate so fast, and therefore the centrifugal force is not so great and does not counteract the radial hydrostatic pressure difference existing in the upper layers. The liquid in contact with the glass bottom is thus forced inwards and carries the precipitate with it.

The phenomena connected with the formation and the disappearance of ice in a large lake, such as Lake George, have interested me for years. One clear night at the end of December, when the water of a large bay was at a uniform temperature of not over 0.2° C. and the air temperature was −22° C., ice, which formed slowly at some places on the shore, melted in a couple of minutes when pushed out a few meters from the shore. There was no wind in the bay, but a slight breeze over the central part of the lake caused a very slow circulation of water in the bay with a velocity of perhaps 1 or 2 cm. per second.

In contrast with this consider the phenomena observed one clear afternoon of the following April. The body of the lake was still covered with ice, which was about 20 cm. thick, but close to the shore there were places where the ice had melted back for a distance of 5 meters or more. Although the air temperature was +3° C. and the water 10 cm. below the surface was at +2.5° C., ice crystals about 50 cm. long formed in these pools in less than half an hour. After considerable analysis I believe I can explain this apparent paradox by the stability in the stratification of the water in April caused by the denser underlying warm water which had been heated by the sun. With this stability which prevented vertical convection the surface water could freeze because of the radiation into the clear sky. But in December the water temperature was so uniform that the differences of density were not sufficient to prevent verticle circulation, and thus the surface could not cool to the freezing point. It appears, then, that a pool of water at +1° C., exposed to cold air with a slight wind, can be made to freeze more rapidly if the water is heated from the bottom. Sometime I want to try this as an experiment.

All hobbies, however, stimulate individual action, and many develop wholesome curiosity. The child should acquire them early, and our educational system should foster them.

Chapter Eight

FLAMES OF ATOMIC HYDROGEN

PART ONE

When a tungsten wire is heated to incandescence in a vacuum by an electric current (as in a vacuum type tungsten lamp) the heat is dissipated almost wholly by radiation, the energy radiated increasing quite accurately in proportion to the 4.7th power of the absolute temperature T. If an inert gas such as nitrogen, argon or mercury vapor is introduced into the bulb at atmospheric pressure a relatively large amount of heat is carried away from the wire by conduction and convection. This energy loss may be determined by subtracting from the total power input the power (in watts) corresponding to the radiation which has previously been measured in the vacuum at the same filament temperature. In this way it was found [1] that the heat loss by conduction and convection increases in proportion to about the 1.9th power of the temperature even up to temperatures as high as the melting point of tungsten (3660 deg. K.).[2] This result was found to be in excellent agreement with a theory of heat convection which was based on the assumption that in the immediate neighborhood of the filament the heat is carried by conduction.

In the case of a tungsten wire in hydrogen [3] the heat loss by conduction and convection increased with about the 1.9th power of the temperature up to only about 1700 deg. K. and then increased much more rapidly. For example, between 2600 deg. and 3400 deg. the heat carried away by hydrogen at atmospheric pressure increased with the 5.0th power of the temperature and with hydrogen at a pressure of 50 mm. of mercury the exponent was even 6.0.

This abnormal behavior of hydrogen suggested that at high temperatures the hydrogen molecules are dissociated into atoms according to the reaction

$$H_2 = 2\,H \tag{1}$$

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[1] Langmuir, *Phys. Rev.*, *34*, 401 (1912).

[2] These temperatures are on the absolute (Kelvin) scale and can be converted to centigrade by subtracting 273 deg.

[3] Langmuir, *Trans. Amer. Electrochem. Soc.*, *20*, 225 (1911), and *Jour. Amer. Chem. Soc.*, *34*, 860 (1912).

with the absorption of a large amount of energy. The enormous heat conductivity of hydrogen at high temperatures (at 3400 deg., about 23 times that of nitrogen) would thus be due to the absorption of energy from the hot wire by the dissociating hydrogen molecules and the liberation of this energy in the cooler gas at a distance from the wire by the recombination of the atoms which diffuse away from the wire.

Confirmation of the view that this effect is due to the formation of hydrogen atoms rather than to the formation of an endothermic polymorphic form of hydrogen, such as H_3 (corresponding to ozone, O_3) was obtained by observation of the fact that the heat loss from filaments at high temperatures is actually greater with low pressures of hydrogen (50 mm.) than with hydrogen at atmospheric pressure. According to the law of mass action, the degree of dissociation of a gas into atoms must be greater at low pressures than at high, whereas the opposite would be true if molecules containing more than two atoms were formed.

Experimental evidence was soon obtained [4] showing that hydrogen at low pressures, when brought into contact with tungsten or platinum wires at 1300 deg. K. or more, acquired entirely new chemical properties which were quite in accord with those to be expected of an atomic form of the element.

It was found that metallic oxides [5] [6] such as WO_3, CuO, Fe_2O_3, ZnO, or PtO_2 in a bulb containing hydrogen at low pressure are rapidly reduced to the metallic state if a tungsten filament in the bulb (or in another bulb connected to it by glass tubing) is heated to a temperature above about 1500 deg. K. Simultaneously the hydrogen in the bulb gradually disappears. Thus the atomic hydrogen produced by the filament can react with certain metallic oxides at room temperature, although molecular hydrogen cannot do so. The atomic hydrogen can also react at ordinary temperature with oxygen or with phosphorus (to form PH_3). This dissociation of the hydrogen by the hot tungsten wire is prevented,[7] however, by even a minute trace of oxygen (or water vapor) if this comes in contact with the wire.

The atomic hydrogen also shows the property of dissolving in platinum [8] at room temperature and causing a marked increase in the electrical resistance of the platinum. Allowing oxygen to come into contact with the platinum brings the resistance back to the normal value.

By a quantitative study of the heat losses from tungsten wires at various temperatures in hydrogen, especially at low pressures, it has been possible to determine the degree of dissociation[9] and the heat of combination of the atoms to form molecules. Since these experiments were made more accurate data for determining the temperatures of tungsten filaments have come into use. G. N. Lewis and M. Randall[10] and others have pointed out that the third law of thermodynamics gives a relation between the heat of dissociation and the degree of dissociation.

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[4] Langmuir, *Jour. Amer. Chem. Soc.*, *34*, 1310 (1913).

[5] Langmuir, *Trans. Amer. Electrochem. Soc.*, *29*, 294–5 (1916).

[6] Langmuir, *General Electric Review*, *16*, 962 (1913).

[7] Langmuir, *Journ. Amer. Chem. Soc.*, *38*, 2271 (1916) ; *Trans. Amer. Electrochem. Soc.*, *29*, 261 (1916) ; *General Electric Review*, *25*, 445 (1922).

[8] Freeman, *Jour. Amer. Chem. Soc.*, *35*, 927 (1913).

With this relationship and the new temperature scale of Forsythe and Worthing,[11] the degree of dissociation of hydrogen has been recalculated from the experimental data of 1914. The results are expressed by the equation

$$\log_{10} K = -\frac{21,200}{T} + 1.765 \log_{10} T - 9.85 \times 10^{-5}\, T - 0.256 \tag{2}$$

where K is the equilibrium constant defined by

$$K = p_1^2/p_2 \tag{3}$$

p_1 being the partial pressure of atomic hydrogen and p_2 the pressure of molecular hydrogen, both expressed in atmospheres. Let x, the degree of dissociation, be expressed as the fraction of the hydrogen molecules which have been dissociated into atoms. Then if P is the total pressure, p_1 and p_2 are given by

$$p_1 = 2Px/(1+x)\,;\; p_2 = (1-x)\,P/(1+x) \tag{4}$$

and the equilibrium constant K in equation (2) is also given by

$$K = 4Px^2/(1-x^2) \tag{5}$$

Table I gives the equilibrium constant K and the degree of dissociation at various temperatures[12] as calculated from equations (2) and (5).

From equation (2), by applying the Clapeyron equation, we can calculate H, the heat absorbed by the dissociation of the molecular hydrogen (at constant pressure), as follows:

$$H = 97{,}000 + 3.5\, T - 0.00045\, T^2 \tag{6}$$

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[9] Langmuir and Mackay, *Jour. Amer. Chem. Soc.*, *36*, 1708 (1914); *37*, 417 (1915); *38*, 1145 (1916).

[10] Lewis and Randall, "Thermodynamics," McGraw-Hill, New York, 1923, page 470.

[11] Forsythe and Worthing, *Astrophys. Jour.*, *61*, 146 (1925).

[12] The revision in the calculation of x in 1915 changed the values of x as follows:

T	Old	New
2000 deg.	0.00165	0.00122
2400 deg.	0.0109	0.0104
2800 deg.	0.0421	0.0488
3200 deg.	0.117	0.154

This is expressed in small calories per gram-molecule of hydrogen (2.016 grams). The heat of reaction at constant volume Q is

$$Q = 97{,}000 + 1.5\,T - 0.00045\,T^2 \tag{7}$$

HEAT CONDUCTIVITY OF HYDROGEN

The dissociation of the hydrogen greatly increases the heat conductivity. First, let us consider the laws governing the rate of loss of heat through hydrogen which is not dissociated appreciably.

It has been shown [1] in this case that the loss of heat by conduction and convection from a body of temperature T_2 in a gas at temperature T_1 is

$$W_c = S\,(\phi_2 - \phi_1) \tag{8}$$

where W_c is expressed for example in watts; S is the shape factor which is independent of the temperature but depends on the size and shape of the body and on the effective thickness of the film of gas which surrounds it. The quantities ϕ_1 and ϕ_2 are expressed as an integral of the heat conductivity k over a temperature range from 0 to T_1, or T_2, thus

$$\phi = \int_0^T k\,dT \tag{9}$$

For high temperatures (T_2) with hydrogen, ϕ_2 is approximately $1.06 \times 10^{-4}\,T_2^{3/2}$ and ϕ_1 at $T_1 = 300$ is 0.3 watts per cm.

The effect of the dissociation of the hydrogen is to increase the heat carried from the body by an amount W_D given by

$$W_D = S\,D\,Q_1\,c \tag{10}$$

where S is the shape factor, D the diffusion coefficient of hydrogen atoms through molecular hydrogen, Q_1 the heat evolved (expressed in watt seconds) when 1 gram of hydrogen atoms combine to form molecules, and c is the concentration (grams per cu. cm.) of the atomic hydrogen at the temperature T_2.

It was found that

$$D = 0.00214\,T_2^{3/2} \tag{11}$$

From equation (7) we see that at temperatures of 2000 deg. or 3000 deg. Q_1 is about 49,000 calories or 205,000 watt-seconds. The value of c, according to equation (4) and the ordinary gas laws, is

$$c = \frac{0.0244}{T_2}\,\frac{Px}{1+x} \tag{12}$$

Substituting these values in (10) we get (for W_D in watts, P in atmos., and S in cm.)

$$W_D = 10.7\ S \sqrt{T_2}\ Px/(1+x) \qquad (13)$$

TABLE I

THE DEGREE OF DISSOCIATION OF HYDROGEN INTO ATOMS

T Deg. K	K Atmos.	x At 1 Atmos.	T Deg. K	K Atmos.	x At 1 Atmos.
300	2.63×10^{-67}	2.56×10^{-34}	2800	9.58×10^{-3}	4.88×10^{-2}
1000	5.50×10^{-17}	3.71×10^{-9}	3000	3.30×10^{-2}	9.03×10^{-2}
1200	2.48×10^{-13}	2.48×10^{-7}	3200	9.78×10^{-2}	0.154
1400	1.04×10^{-10}	5.08×10^{-6}	3400	0.256	0.245
1600	9.81×10^{-9}	4.95×10^{-5}	3600	0.598	0.361
1800	3.42×10^{-7}	2.92×10^{-4}	3800	1.24	0.488
2000	5.93×10^{-6}	1.22×10^{-3}	4000	2.56	0.625
2100	2.02×10^{-5}	2.24×10^{-3}	4500	10.9	0.855
2200	6.18×10^{-5}	3.92×10^{-3}	5000	34.7	0.9469
2300	1.71×10^{-4}	6.54×10^{-3}	6000	169.0	0.9884
2400	4.36×10^{-4}	1.04×10^{-2}	7000	649.0	0.9969
2500	1.04×10^{-3}	1.61×10^{-2}	8000	1560.0	0.9987
2600	2.30×10^{-3}	2.40×10^{-2}	9000	3030.0	0.9993
2700	4.82×10^{-3}	3.48×10^{-2}	10000	5000.0	0.9996

At $T_2 = 3600$ deg. and one atmosphere, $x = 0.361$ and W_D is then 170 S, while from (8) we find at this temperature that W_c is 22.4 S. Thus the heat conductivity of the hydrogen between 3600 deg. and 300 deg. is increased 8.6 fold by the dissociation. At 5000 deg. the factor is about 11.

ARCS IN HYDROGEN AT LOW PRESSURES

In attempting to obtain the Balmer spectrum of hydrogen without contamination by the secondary spectrum, R. W. Wood[13] built very long vacuum tubes of moderate bore, in which he passed currents as large as 20 amperes through moist hydrogen at about 0.5 mm. pressure. He observed many remarkable phenomena. Short pieces of tungsten wire projecting into the discharge were heated to incandescence, although a fine thread of glass or a platinum wire in a similar position was apparently not heated by the discharge. On drying the hydrogen with phosphorus pentoxide the secondary spectrum (due to molecular hydrogen) appeared strongly and the Balmer spectrum (due to atomic hydrogen) nearly disappeared. The heating of the tungsten wire was also prevented by drying the hydrogen.

In correspondence with Professor Wood the writer had suggested[13] that the effect of moisture is to poison the catalytic activity of the dry glass surfaces that otherwise converted atomic into molecular hydrogen. Thus with moist hydrogen the tube became filled with nearly pure atomic hydrogen and the diffusion of this to the catalytically active tungsten wire caused the heating of the latter. Calculations based on an equation like (13) proved that a pressure of only 0.16 mm. of atomic hydrogen at 500 deg. C. would suffice to maintain a tungsten filament at 2400 deg. K.

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[13] R. W. Wood, *Proc. Roy Soc.*, *102*, 1 (1922) and *Phil. Mag.*, *44*, 538 (1922).

These conclusions were confirmed by Wood's observations that the walls of the tube became only slightly heated if the hydrogen was moist, whereas they were strongly heated with dry hydrogen. A tungsten wire was heated red hot even when mounted in a side tube (of 5 mm. diameter) at a distance of 4 cm. from the discharge tube, showing that the hydrogen atoms could diffuse in relatively large quantities out of the discharge.

It occurred to the writer that it should be possible to obtain even higher concentrations of atomic hydrogen by passing powerful electric arcs between tungsten electrodes in hydrogen at atmospheric pressure and by blowing atomic hydrogen out of the arc by a jet of hydrogen directed against it.

ARCS IN HYDROGEN AT ATMOSPHERIC PRESSURES

Studies had been made several years ago in this laboratory of arcs between tungsten electrodes in various gases.[14] Arcs in hydrogen were remarkable because of the high voltage drop and small cross-section. A 10-amp., direct-current arc between heavy tungsten electrodes about 7 mm. apart in a bulb containing pure hydrogen at atmospheric pressure appeared as a sharply defined brilliant red line about 0.5 mm. in diameter along which the potential gradient was 150 volts per cm., this being about 15 times as great as in nitrogen or argon. This abnormal behavior of hydrogen was attributed to the dissociation which carried energy so rapidly out of the arc.

A simple analysis shows that ordinary heat conduction (i.e., without dissociation) and even convection are entirely incapable of causing such a flow of heat as 1500 watts per cm. of length of arc. For the flow of heat between concentric cylinders of radii a and r the shape factor S in equation (8) has the value

$$S = \frac{2\pi l}{\log (a/r)} \tag{14}$$

where l is the length of the cylinder. The surfaces of equal temperature which surround the arc are concentric cylinders. Let us consider the two surfaces which are the loci of points having the temperatures 2000 deg. and 1000 deg., respectively. The value of $(\phi_2 - \phi_1)$ corresponding to these temperatures is 5.6 watts per cm. Substituting this in equation (8) together with $W_D = 1500\,l$ watts. we obtain $S = 267$ cm.

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[14] G. M. J. Mackay and C. V. Ferguson, *J. Franklin Inst., 181,* 209 (1916).

From equation (14) we see that a/r must then be 1.027. In other words if the heat is to be carried by ordinary conduction the temperature would have to drop from 2000 deg. to 1000 deg. within a region in which the radius increases by less than 3 per cent. For the heat to travel any reasonable distance from the arc by ordinary conduction would require a temperature drop of the order of 50,000 deg.

Heat Carried by Convection

To form a conception of the heat that can be carried from bodies at very high temperatures by convection currents in a gas, let us consider a stream of gas of cross-section A moving through a heated region having a temperature T_2. Let T_1 be the temperature of the gas before entering the hot region and v be the velocity of the gas while in the hot region. The number of gram-molecules of gas passing the hot region per second is then $Avp/(RT_2)$ where p is the pressure in bars and R is the gas constant (83.7×10^4 ergs per deg.). If C is the specific heat of the gas per gram-molecule expressed in joules per deg. (for hydrogen up to 2000 deg. C may be taken to be $7.5 \times 4.2 = 31.6$) we thus find that the rate at which the heat is carried from the hot region (in watts) is

$$W = A\,v\,p\,C\,(T_2 - T_1)/(RT_2) \tag{15}$$

To maintain the convection current through the hot region requires the action of a force equal to the product of the velocity v by the mass of gas which moves per second through the hot region. We thus find that the pressure difference Δp needed to maintain the movement of the gas is

$$\Delta p = M\,p\,v^2/(RT_2) \tag{16}$$

where M is the molecular weight of the gas (2 for hydrogen).

The available pressure difference in the gas near a heated body may be looked upon as due to the difference in pressure between two columns of gas of height h and of temperatures T_2 and T_1, respectively. Thus we find that

$$\Delta p = \frac{M\,p\,h\,g}{RT_2}\,\frac{T_2 - T_2}{T_1} \tag{17}$$

where g is the acceleration of gravity (980 cm. per sec.^{2}). From equations (16) and (17) we find that the velocity of the gas in the heated region is given by

$$v^2 = hg\,(T_2 - T_1)/T_1 \tag{18}$$

This must be looked upon as an upper limit to the velocity of convection currents in any gas, for the effect of viscosity, which we have neglected, must decrease the velocity below the value given by (18). It is interesting to note that this limiting velocity is the same for gases of different densities. As an illustration let us take a case where $h = 5$ cm., $T_2 = 2000$ deg., and $T_1 = 300$ deg. We find that the velocities then cannot exceed 166 cm. per sec. The actual velocities set up by convection currents are probably less than 1/5th of this.

Combining (18) and (15) and neglecting T_1 compared to T_2 in the factor $T_2 - T_1$, we find as an upper limit to the heat that can be carried by convection currents

$$W = A\, p\, C \sqrt{hg\, T_2/T_1}/R$$

For hydrogen at atmospheric pressure this reduces to

$$W = 12 \times A \sqrt{h\, T_2/T_1} \text{ watts.}$$

Thus with $h = 5$, $T_2 = 2000$ deg. and $T_1 = 300$ deg. we find $W = 60\, A$, which means that the maximum heat that can be carried by a convection current (at 2000 deg.) is only 60 watts per sq. cm. It is evident that convection currents of molecular hydrogen are entirely inadequate as a means of carrying away the 1500 watts per cm. of length that were observed in the hydrogen arc.

HEAT CARRIED BY DIFFUSION OF HYDROGEN ATOMS

Let us now consider whether the observed energy loss can be explained as due to the diffusion of hydrogen atoms. Assuming that the hydrogen in the arc is completely dissociated, we place in equation (13): $x = 1$, $P = 1$ atmosphere, and $W_D = 1500\, l$, and thus find

$$S\sqrt{T_2} = 280\, l$$

and from (14)

$$\log\, (a/r) = 0.0224\, \sqrt{T_2}$$

The temperature T_2 enters this equation only because the diffusion coefficient and the density of the atomic hydrogen vary with the temperature. It is thus reasonable to put for T_2 the temperature at which the hydrogen is about half dissociated even if the temperature in the arc itself is much greater than this. Thus putting $T_2 = 3800$ deg. we find $a/r = 4$.

From the derivation of the equations we see that the radii a and r correspond to places where $x = 0$ and $x = 1$, respectively. The diameter of the arc was observed to be 0.5 mm. Suppose the temperature at the surface of the arc is 10,000 deg. Then between this surface and the surface at which the temperature is 5000 deg. the heat cannot be carried by diffusion of hydrogen atoms, for even at the lower of these temperatures the dissociation is nearly complete and there is thus no concentration gradient. Let us assume that heat is carried in this region by conductivity through atomic hydrogen gas. From the principles of the kinetic theory we can calculate for a monatomic gas of atomic weight M at very high temperatures that

$$\phi = 5.6 \times 10^{-20}\ T^{3/2}/(\sigma^2\sqrt{M})$$

where σ is the diameter of the atoms of the gas. Taking $\sigma = 1.3 \times 10^{-8}$ cm. as a reasonable estimate of the diameter of the hydrogen atom, we find for atomic hydrogen

$$\phi = 3.3 \times 10^{-4}\ T^{3/2}$$

Placing $T_2 = 10{,}000$ and $T_1 = 5{,}000$ we find $\phi_2 - \phi_1 = 215$ watts per cm. and thus from the value of W_D we find by equations (10) and (14) that a/r is 3.0. Thus between a cylinder of 0.5 mm. and one of 1.5 mm. diameter 1500 watts per cm. can be conducted by the atomic hydrogen with a drop in temperature from 10,000 deg. down to 5000 deg. From this cylinder of 1.5 mm. the diffusion of atomic hydrogen could carry the energy out to one of 6.0 mm. diameter, while the temperature falls to a point where there is little dissociation (say 2000 deg.).

Thus the diffusion of atoms from the arc is an adequate mechanism for carrying the energy out to a distance of 3 mm. from the arc. We still have to explain how the heat can be transferred from this point to the bulb. We have seen that neither convection nor conduction through the molecular hydrogen can carry this amount of energy.

We are therefore forced to the conclusion that in this arc the heat was delivered by the atomic hydrogen directly to the heavy tungsten electrodes. The length of the arc was only 7 mm. and one of the electrodes was a solid piece of tungsten about 15 mm. in diameter.[15]

We must also conclude that the high energy of 1500 watts per cm. was only possible in this arc because of the proximity of the mass of tungsten.

PRELIMINARY EXPERIMENTS WITH FLAMES OF ATOMIC HYDROGEN

To try out the possibility of blowing atomic hydrogen out of an arc, 20-amp, arcs from a constant-current transformer were passed between two tungsten rods 6 mm. in diameter mounted transversely in a horizontal alundum tube (10 cm. diameter) through which a stream of hydrogen flowed. With voltages from 300 to 800, arcs could be maintained with electrode separations up to 2 cm. The magnetic field of the arc caused it to move transversely so that it became fan shaped. Iron rods 2 or 3 mm. in diameter melted within one or two seconds when they were held 3 to 5 cm. above the arc.

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[15] A photograph of this arc, showing the electrodes, is given in Mackay and Ferguson's article. See reference 14.

By directing a jet of hydrogen from a small tube into the arc, the atomic hydrogen could be blown out of the arc and formed an intensely hot flame. To maintain the arc in a stable condition the electrodes were brought closer together (1 to 3 mm.) but the arc did not remain entirely between the electrodes, but extended as a fan to a distance of 5 to 8 mm. The flame of atomic hydrogen, however, extended far beyond the arc. At distances of 1 or 2 cm. from the arc molybdenum (melting point 2900 deg. K.) melted with ease. Near the edge of the arc tungsten rods (m. p. 3660 deg. K.) could be melted. Quartz melted with much more difficulty than molybdenum, indicating that the extreme rapidity of heating of the metals was partly due to their catalytic action in causing the atoms to combine on their surface.

The use of hydrogen under these conditions for melting metals has proved to have many advantages. Iron can be melted without contamination by carbon, oxygen or nitrogen. Because of the powerful reducing action of the atomic hydrogen, alloys containing chromium, aluminum, silicon or manganese can be melted without fluxes and without surface oxidation. With these flames of atomic hydrogen even fairly large pieces of aluminum oxide, Al_2O_3, magnesium oxide, MgO, or thorium oxide, ThO_2 can be melted with ease. The oxides thus heated show no apparent reduction to metal, perhaps because any metal that is formed is volatilized at these high temperatures.

The technical development of methods for utilizing flames of atomic hydrogen has been the work of several men, among whom Robert Palmer and R. A. Weinman should be particularly mentioned.

An article by Mr. Weinman and the writer describes the application of these flames to the welding of metals.

THE TEMPERATURE OF THE ATOMIC HYDROGEN FLAME AS COMPARED TO OTHER FLAMES

Let us suppose we could obtain atomic hydrogen in bulk at atmospheric pressure and room temperature and that we could then let this "burn" to the molecular form in a flame. What would be the temperature of this flame and how would it compare with that of other flames? Taking the heat of reaction (for 2 grams) to be 98,000 calories and taking the specific heat of molecular hydrogen (for 2 grams) to be $6.5 + 0.0009T$, we find that the heat of the reaction would be sufficient to heat the hydrogen to 9200 deg. K.

A similar calculation[16] for the oxy-hydrogen flame gives a temperature of 3700 deg. K. and for the oxy-acetylene flame about 7000 deg. K. Of course at such high temperatures as these the products of the combustion would be largely dissociated so that the full heat of the reaction would not be available, and the flame temperatures are therefore much lower. For the case of the atomic hydrogen flame we find

$$(1 - x)\, H_0 = [2\, x\, C_1 + (1 - x)\, C_2]\, T$$

where T is the temperature of the flame and x the degree of dissociation at this temperature; C_1 and C_2 are the mean specific heats of the atoms and molecules, respectively. By trial, using the values of x from Table I, we find that the equation is satisfied if we take $T = 3990$ deg. K.; the degree of dissociation, x, at this temperature is 0.62. Similar calculations for the other flames, taking into account the degree of dissociation[17] of the water vapor and carbon dioxide, give for the oxy-hydrogen flame $T = 3370$ deg. K. and $x = 0.20$. For the oxy-acetylene flame $T = 3750$ deg., at which temperature the water vapor is about 38 per cent and the carbon dioxide about 89 per cent dissociated.

These temperatures for the oxy-hydrogen and oxy-acetylene flames are still too high, since the hydrogen (and probably the oxygen) in the partly dissociated products of combustion at these high temperatures must be largely dissociated into atoms. The effect of this will be to increase the degree of dissociation of the H_2O and CO_2 beyond that taken into account in the calculation. An error of this kind, however, does not occur in the calculation of the temperature of the atomic hydrogen flame. Thus the calculations indicate that an atomic hydrogen flame is far hotter than either the oxy-hydrogen or the oxy-acetylene flame.

There is another factor which tends greatly to increase the temperature of the atomic hydrogen flame even above the calculated value of 4000 deg. The atomic hydrogen, instead of being originally at room temperature, is already at a high temperature at the moment of its escape from the arc. The conditions are analogous to those in an oxy-hydrogen flame in which both gases are preheated. Thus the upper limit of temperature is fixed only by the degree of dissociation of the hydrogen and the rate at which heat is lost by radiation or contact with bodies of lower temperature.

The fact that the degree of dissociation of hydrogen into atoms is very much less at a given temperature than that of carbon dioxide into oxygen and carbon monoxide is an important factor making the atomic hydrogen flame much hotter than the oxy-acetylene flame.

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[16] The specific heats for these calculations were taken from a table given on p. 80 of Lewis and Randall's "Thermodynamics."

[17] Langmuir, *Jour. Amer. Chem. Soc., 28,* 1378 (1906).

The rate at which energy may be delivered to a surface by atomic hydrogen can be calculated readily by equation (13). Let us consider that a flame or stream of atomic hydrogen is directed against a plane metallic surface which is at a temperature of less than 2000 deg. and which catalyzes the combination of atoms. Thus at the surface the concentration of atoms is practically zero. At a distance of 5 mm. from the surface let us assume that the degree of dissociation is 0.50 and the temperature is 4000 deg. The shape factor S in equation (13) is the area of the surface divided by the thickness through which diffusion occurs. Thus we find that the energy is delivered to the surface at the rate of 450 watts per cm^2, which is 25 per cent greater than that radiated from a tungsten surface at its melting point (3660 deg. K.). The rate of diffusion of atomic hydrogen is therefore so great that it is not necessary, for the rapid melting of metals, that the blast of gas from the flame should carry the atomic hydrogen closer than about 5 mm. from the surface.

A stream of molecular hydrogen of 100 cc. per second (about 12 cubic feet per hour) measured at room temperature, if converted to atomic hydrogen at 5000 deg. ($x = 0.95$) would be capable of supplying energy at the rate of about 1.6 kw. These figures may help to give more concrete ideas as to the manner in which atomic hydrogen can be used for the melting or welding of metals.

It may be of interest to compare some features of the atomic hydrogen arc process with the process described by Mr. Alexander. In the latter process conducting vapor is ordinarily produced at the electrodes and enters the arc. The heat delivered to the weld is in large part due to anode and cathode potential drops where the arc leaves the electrode and enters the metal. Atomic hydrogen produced in the arc and at its surface carries heat from the arc (and thereby raises the voltage) to the surface of the metal and contributes greatly to the speed of welding. The atomic hydrogen is also of great value in reducing oxides and thus makes possible the arc welding of alloys containing chromium, manganese, silicon, etc. The function of the hydrogen in neutralizing the action of small admixtures of air is not necessarily dependent on the presence of atomic hydrogen.

By adjusting the position of the flame with respect to the surface the rate of melting is under accurate control in the atomic hydrogen flame process, and this feature makes it possible to weld very thin sheet metals or other objects of small size.

It may seem at first sight peculiar that the addition of nitrogen to the hydrogen decreases the arc drop in the process described by Mr. Alexander whereas it increases it when the atomic hydrogen torch is used. In the first case, however, the arc is carried largely through conducting vapor, the arc is short and its length is not modified by the composition of the surrounding gas. The addition of nitrogen decreases the heat conductivity of the gas because of the decreased production of atomic hydrogen, and thus the voltage is lowered since less heat is withdrawn from the arc. In the second case, the decreased voltage drop per unit length along the arc is more than compensated for by the increased length of the arc which is brought about by the addition of nitrogen. The lower mobility of ions in the heavier gas probably causes the arc to be carried forward more easily by the blast of gas and thus increases its length.

PART TWO

A STUDY OF the heat losses from tungsten filaments at very high temperatures in at atmosphere of hydrogen led the writer to conclude in 1911 [1] that hydrogen is largely dissociated into atoms at temperatures of 2500°K or more. The total heat loss from the filament, after subtracting that due to radiation, increased in proportion to the 7th power of the temperature at temperatures over 2700°K, whereas the normal heat loss by convection, as determined for example in nitrogen, should have increased with the 1.8th power of the temperature. Further work showed [2] that by heating a platinum or tungsten filament above 1300°K in hydrogen at low pressures, atomic hydrogen was formed which had very remarkable properties. It would dissolve at ordinary temperatures in platinum and would be condensed on glass surfaces at room temperature and at this temperature combined instantly with oxygen or phosphorus and reduced oxides such as WO_3, CuO, Fe_2O_3, ZnO or PtO_2. More accurate measurements of the heat losses from tungsten filaments in hydrogen at various pressures [3] gave 90,000 small calories as the heat of combination of 2 grams of atomic hydrogen, and showed that the degree of dissociation at atmospheric pressure increased from about 2 per cent at 2400°K to about 34 per cent at the melting point of tungsten.

In attempting to obtain the Balmer spectrum of hydrogen without contamination by the secondary spectrum, R. W. Wood [4] built very long vacuum tubes in which he passed currents of amperes through moist hydrogen at a few millimeters pressure. He observed many remarkable phenomena. Short pieces of tungsten or platinum wire mounted in a side tube became heated to incandescence, although no electric current flowed through this tube and the glass walls near the wires were not heated strongly. These effects were nearly absent when the hydrogen was carefully dried. In correspondence with Professor Wood, the writer suggested that these effects were due to high concentrations of atomic hydrogen which could accumulate in the tube because of the effect of water vapor in poisoning the catalytic activity of dry glass surfaces that otherwise destroyed the atomic hydrogen. With moisture present the atomic hydrogen diffused through the side tube and the atoms combined to form molecules on the surfaces of the metallic wires which acted as catalysts.

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[1] Langmuir, *Trans. Amer. Electrochem. Soc., 20,* 225 (1911) and *Jour. Amer. Chem. Soc., 34,* 860 (1912).

[2] Langmuir, *Jour. Amer. Chem. Soc., 34,* 1310 (1912); Freeman, *Jour. Amer. Chem. Soc., 35,* 927 (1913).

[3] Langmuir and Mackay, *Jour. Amer. Chem. Soc., 36,* 1708 (1914), *37,* 417 (1915) and *38,* 1145 (1916).

[4] R. W. Wood, *Phil. Mag., 44,* 538 (1922).

Shortly after this correspondence it occurred to the writer that it should be possible to obtain even higher concentrations of atomic hydrogen by passing powerful electric arcs between tungsten electrodes in hydrogen at atmospheric pressure. The high heat conductivity of the gas due to the energy liberated by the recombination of the rapidly diffusing atoms should prove of particular value in the construction of electric furnaces, and for melting metals in general. Experiments of this kind were soon made. Twenty ampere arcs from a constant current transformer were passed between two tungsten rods 6 mm. in diameter mounted transversely in an alundum tube (10 cm. diam.) through which a stream of hydrogen flowed and burned at the open end.

Arcs up to 2. cm. in length were obtained with voltages ranging from 300–800. The arc, of a beautiful red color, was of small diameter (about 3 mm.) and was bowed out into a fan shape by its own magnetic field.

Iron rods 2 or 3 mm. in diameter melted within a couple of seconds when they were held 3–5 cm. above the arc. By directing a jet of hydrogen from a small tube into the arc, the atomic hydrogen could be blown out of the arc and formed an intensely hot flame of atomic hydrogen burning to the molecular form and liberating 90,000 calories per gram molecule—about 50 per cent more than that in an oxy-hydrogen flame. To maintain these conditions the electrodes had to be brought closer together (preferably 1–3 mm.).

In this flame, even at distances of 1 to 2 cm. from the arc, it was found that molybdenum melted with ease, and tungsten rods of 3 mm. diameter could be melted when held very close to the arc itself. Quartz, on the other hand, melted with more difficulty than molybdenum, indicating that the catalytic action of the metals played an important part in the rapidity with which they could be heated.

The use of hydrogen under these conditions for melting metals has proved to have many advantages. Iron can be welded or melted without contamination by carbon, oxygen or nitrogen. Because of the powerful reducing action of the atomic hydrogen, alloys containing chromium, aluminum, silicon or manganese can be welded without fluxes without surface oxidation. The rapidity with which such metals as iron can be melted seems to exceed that in the oxy-acetylene flame. so that the process promises to be particularly valuable for welding.

The technical development of these welding processes using flames of atomic hydrogen has been the work of several men, among whom Robert Palmer and R. A. Weinman must be particularly mentioned. Papers describing the apparatus used and the results obtained will soon be published by Mr. Weinman and the writer in the *General Electric Review.*

Mr. P. Alexander, following out a line of development suggested by Professor Elihu Thomson, has independently arrived at an arc welding process utilizing hydrogen for the purpose of improving the ductility of the weld and the speed of operation. In this process the arc is passed between an iron electrode and the material to be welded. This process also depends at least in part on the use of the high heat conductivity of atomic hydrogen.

Some joint work of Mr. Alexander and the writer has shown that particular advantages are obtained in some cases by using mixtures of nitrogen and hydrogen, and that the quality of the weld is not impaired by nitrogen unless oxygen is also present. A paper by Mr. Alexander describing his process will appear simultaneously with those dealing with the atomic flame process.

PART THREE [1,2]

The heat carried away from an incandescent wire by a surrounding inert gas at ordinary temperatures increases roughly in proportion to the 1.9th power of the absolute temperature, T, of the filament.[2] This relation holds, for example, for such gases as nitrogen, argon, and mercury vapor up to the temperature of melting tungsten, 3660° K. In the case of hydrogen, however, abnormal results were obtained in experiments made at high temperatures. Up to about 1700° K. the normal exponent of 1.9 was observed, but at higher temperatures the exponent increased until at 2600° K. and above it was about 5.0. At 3400° K. the heat conducted by hydrogen was twenty-three times as great as that carried by nitrogen under similar conditions.

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[1] Received April 19, 1927. A major part of the subject matter of this paper was covered in an address under the same title delivered at the General Meeting of the American Chemical Society, Philadelphia, Pa., September 8, 1926. Preliminary publications have appeared in the *Gen. Elec. Rev., 29,* 153, 160 (1926).

[2] Langmuir, *Trans. Am. Electrochem. Soc.,* 20, 225 (1911) ; *Phys. Rev., 34,* 401 (1912) ; *Jour. Amer. Chem. Soc., 34,* 860 (1912).

Nernst[3] in 1904 had developed the theory of heat conduction in a dissociating gas and had shown that dissociation results in a great increase in the heat conductivity. The dissociation products diffuse from the hot portions of the gas into the cold portions and there, by recombining, give up the large energy of the chemical reaction. This suggested that the abnormal heat conductivity of hydrogen at high temperatures is due to dissociation of the hydrogen into atoms according to the reaction

$$H_2 = 2H \qquad (1)$$

An abnormal heat conductivity might, however, be due to the formation of an endothermic polymorphic form of hydrogen such as H_3, corresponding, for example, to ozone. According to the law of mass action, the degree of dissociation of a gas into atoms must be greater at low pressures than at high, whereas the opposite would be true if molecules containing more than two atoms were formed.

At temperatures below 1700° K. the heat carried away by convection and conduction was greater at higher pressures of hydrogen than at lower pressures. For example, a wire of 0.0706 mm. diameter at 1500° K. dissipated over twice as much energy in hydrogen at 760 mm. as in hydrogen at 50 mm. pressure. At temperatures above 2700° K., however, more energy was dissipated at 50 mm. than at 760 mm. There are evidently two factors acting in opposite directions. Since the heat loss by convection and normal conduction increased with temperature according to a law which had been determined, it was possible to extrapolate to the higher tem-

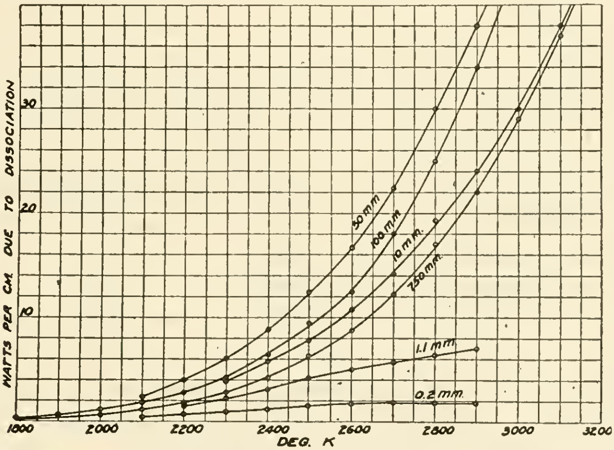

FIG. 1.—Heat Loss from a Tungsten Filament Due to Dissociation of Hydrogen by Filament in Hydrogen at Various Pressures.

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[3] Boltzmann Festschrift, p. 904 (1904).

peratures, and then by subtracting this from the observed heat loss at the higher temperatures it was possible to find the energy that was carried from the filament by the dissociation (or association) that occurred. A portion of the data obtained in this way with a filament of 0.0706 mm. diameter at a series of different pressures is given in Figure 1.[4]

At temperatures from 2000° to 2400° K. more than twice as much heat is carried in this way from the filament in hydrogen at 50 mm. pressure as at 760 mm., but data beyond the range included in the diagram show that this ratio falls to 1.55 at a filament temperature of 3400° K. At pressures still lower than 50 mm. the heat loss does not continue to increase as the pressure is lowered, but calculation shows that this is due to the fact that the free path of the gas molecules is no longer negligible compared with the diameter of the wire so that there is a "concentration drop" of the modified hydrogen at the surface of the wire analogous to the temperature drop discovered by Smoluchowski.

The marked increase in heat loss as the pressure was lowered proved that the heat was carried from the filament by a dissociation of the hydrogen into atoms. In fact, the amount of the increase was in quantitative agreement with a mathematical theory of the effect based on an assumed dissociation.

When the pressure was lowered to 10, 1.1, and 0.2 mm. the heat loss decreased with decreasing pressure (Figure 1), and decreased much more rapidly at the high temperatures than at the lower ones, so that finally (at 0.21, 0.04, and 0.015 mm.) it became independent of the filament temperature at temperatures above 2600° K. This indicates that the dissociation under these conditions is nearly complete, so that the rate of dissociation, which determines the heat loss, is limited only by the rate at which the molecules strike the surface of the wire. Quantitative calculations based on the kinetic theory confirmed this conclusion.

By means of these theoretical considerations it was possible to determine the degree of dissociation and the heat of the reaction by which atoms combine to form molecules. The results that were published in 1915 gave 90,000 calories as the heat of combination of 2 grams of hydrogen atoms at constant pressure and at 3000° K. The degree of dissociation,[5] x, expressed as the fraction of the molecules which have been dissociated, was found to be, at atmospheric pressure, 0.00165 at 2000° K., 0.0109 at 2400° K., and 0.0421 at 2800° K.

Since these experiments were made, more accurate data for determining the temperatures of tungsten filaments have come into use. G. N. Lewis and M. Randall[6] and others have pointed out that the third law of thermodynamics gives a relation between the heat of dissociation and the degree of dissociation.

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[4] Langmuir and Mackay, *Jour. Amer. Chem. Soc., 36*, 1708 (1914).

[5] Langmuir, *Ibid., 37*, 417 (1915); *38*, 1145 (1916).

DEGREE OF HYDROGEN DISSOCIATION

With this relationship and the new temperature scale of Forsythe and Worthing,[7] the degree of dissociation of hydrogen has been recalculated from the experimental data of 1914. The results are expressed by the equation

$$\log_{10} K = -\frac{21{,}200}{T} + 1.765 \log_{10} T - 9.85 \times 10^{-5} T - 0.256 \qquad (2)$$

where K is the equilibrium constant defined by

$$K = p_1^2/p_2 \qquad (3)$$

p_1 being the partial pressure of atomic hydrogen and p_2 the pressure of molecular hydrogen, both expressed in atmospheres. Then if P is the total pressure, p_1 and p_2 are given by

$$p_1 = 2Px/(1+x)\,;\; p_2 = (1-x)\,P/(1+x) \qquad (4)$$

where x is the degree of dissociation.

The equilibrium constant K in equation (2) is also given by

$$K = 4Px^2/(1-x^2) \qquad (5)$$

Table I gives the equilibrium constant K and the degree of dissociation at various temperatures as calculated from equations (2) and (5).

Note—This revision in the calculation of x changed the values of x calculated in 1915 to the following values:

T (°K.)	Old	New
2000	0.00165	0.00122
2400	0.0109	0.0104
2800	0.0421	0.0488
3200	0.117	0.154

From equation (2), by applying the Clapeyron equation, we can calculate H, the heat absorbed by the dissociation of the molecular hydrogen (at constant pressure), as follows:

$$H = 97{,}000 + 3.5\,T - 0.00045\,T^2 \qquad (6)$$

This is expressed in small calories per gram-molecule of hydrogen (2.016 grams). The heat of reaction Q at constant volume is

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[6] "Thermodynamics," p. 470, McGraw-Hill Book Co., New York, 1923.

[7] *Astrophys. Jour.*, *61*, 146 (1925).

$$Q = 97{,}000 + 1.5\,T - 0.00045\,T^2 \qquad (7)$$

Note—This result for the heat of dissociation which was published in March, 1926,[1] is in excellent agreement with the value 98,570, subsequently found by Witmer[8] from studies of a hydrogen band spectrum found by Lyman. In a later paper[9] from a more careful analysis of similar data Witmer concludes that Q_0 is 100,000 ± 5000 calories.

TABLE I

Degree of Dissociation of Hydrogen into Atoms

T ° K.	K Atmos.	x (At 1 atmos.)	T ° K.	K Atmos.	x (At 1 atmos.)
300	2.63×10^{-67}	2.56×10^{-34}	2800	9.58×10^{-3}	4.88×10^{-2}
1000	5.50×10^{-17}	3.71×10^{-9}	3000	3.30×10^{-2}	9.03×10^{-2}
1200	2.48×10^{-13}	2.48×10^{-7}	3200	9.78×10^{-2}	0.154
1400	1.04×10^{-10}	5.08×10^{-6}	3400	0.256	0.245
1600	9.81×10^{-9}	4.95×10^{-5}	3600	0.598	0.361
1800	3.42×10^{-7}	2.92×10^{-4}	3800	1.24	0.488
2000	5.93×10^{-6}	1.22×10^{-3}	4000	2.56	0.625
2100	2.02×10^{-5}	2.24×10^{-3}	4500	10.9	0.855
2200	6.18×10^{-5}	3.92×10^{-3}	5000	34.7	0.9469
2300	1.71×10^{-4}	6.54×10^{-3}	6000	169.0	0.9884
2400	4.36×10^{-4}	1.04×10^{-2}	7000	649.0	0.9969
2500	1.04×10^{-3}	1.61×10^{-2}	8000	1560.0	0.9987
2600	2.30×10^{-3}	2.40×10^{-2}	9000	3030.0	0.9993
2700	4.82×10^{-3}	3.48×10^{-2}	10000	5000.0	0.9996

CHEMICAL PROPERTIES OF ATOMIC HYDROGEN

While the measurements of the heat losses from filaments in hydrogen were being made, other experiments[10] showed that hydrogen which had been in contact with heated filaments acquired entirely new chemical properties, and they were quite in accord with those to be expected of an atomic form of the element.

If a tungsten or platinum filament is heated to 1300° K. or more in dry hydrogen at low pressures, preferably less than 1 mm., a limited amount of the hydrogen gradually disappears or cleans up. When the limiting clean-up has taken place no additional clean-up occurs if a second filament is lighted, so we know that the gas is not absorbed by the filament. It was found that part of the hydrogen can be recovered by heating the bulb. The amount of hydrogen that can be cleaned up increases considerably, but not indefinitely, when the bulb is kept cooled by liquid air. If the liquid air is removed after the filament has been allowed to cool, the excess of absorbed hydrogen is evolved but does not recondense when the liquid air is replaced unless the filament is again lighted. The hydrogen on the bulb is thus not in the form of liquefied or solidified atomic hydrogen, but is held there rather as an adsorbed film. Hydrogen atoms striking a bare glass surface can condense, but if they strike atoms already on the surface they combine with these and the molecules escape.

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[8] *Proc. Natl. Acad. Sci., 12,* 238 (1926).
[9] *Phys. Rev., 28,* 1233 (1926).
[10] Langmuir, *Jour. Amer. Chem. Soc., 34,* 1310 (1912).

The maximum amount of hydrogen that can be adsorbed by glass cooled in liquid air was found to be 0.03 cu. mm. per sq. cm., the hydrogen being measured at atmospheric pressure and temperature. This corresponds to 1.5×10^{15} atoms per sq. cm. If these are arranged in a close-packed lattice on the surface their distance between centers would be 2.78×10^{-8} cm. The diameter of the electron orbit in the Bohr hydrogen atom is 1.06×10^{-8} cm. This result confirms the theory that impinging hydrogen atoms combine with adsorbed hydrogen atoms which they strike. If the glass surface is allowed to warm up to room temperature some of the atoms can react with adjacent atoms and thus escape as molecules.

The atomic hydrogen adsorbed on glass is capable of reacting rapidly with oxygen at room temperature and slowly even at liquid-air temperature. Thus if hydrogen is cleaned up by a heated filament on to a bulb cooled in liquid air, and oxygen is admitted after cooling the filament, the oxygen disappears very slowly; but when the liquid air is removed an amount of oxygen suddenly disappears which is the chemical equivalent of the hydrogen that was previously cleaned up. This removal of the adsorbed hydrogen makes it then possible to clean up another portion of hydrogen on to the bulb when the filament is lighted.

Atomic hydrogen from a filament in hydrogen at low pressure, even after diffusing through several feet of glass tubing at room temperature, can manifest itself by reducing such metallic oxides as WO_3, CuO, Fe_2O_3, ZnO, or PtO_2.[11] The blackening of WO_3 or ZnO thus serves as a means for detecting atomic hydrogen. An oxidized piece of copper rapidly acquires a metallic luster. The fact that the atoms can pass through a long crooked tube proves that adsorbed hydrogen atoms can evaporate from glass surfaces at room temperature. Experiments showed that no atomic hydrogen passed through a trap cooled in liquid air, so that at this temperature the evaporation of the atomic hydrogen does not occur. A plug of glass wool in a tube at room temperature also stops the passage of the atoms.

A well-exhausted tungsten filament lamp was connected through a glass tube to a Hale-Pirani vacuum manometer [12] which contained pure platinum wire 0.028 mm. in diameter and 45 cm. long heated to about 125° C. by the passage of a current of 0.0092 ampere. The resistance of the platinum wire was used to measure the pressure of the residual gas in the lamp. After the lamp had run about 50 hours at normal efficiency (2400° K.) the resistance of the platinum wire had *increased* 0.12 ohm, the original resistance having been about 96 ohms. Investigation showed that this increase of 0.125 per cent in resistance was caused by atomic hydrogen which diffused into the platinum wire. The increase in resistance persisted for days after the tungsten filament was turned off, but the resistance returned to normal either after heating the platinum wire or after admitting a little oxygen and then pumping it out again, the platinum wire being kept at 125° C.

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[11] Langmuir, *Proc. Amer. Inst. Elec. Eng., 32,* 1894 (1913); *Trans. Amer. Electrochem. Soc., 29,* 294 (1916).

[12] Hale, *Trans. Amer. Electrochem. Soc., 20,* 243 (1911).

The dissociation of hydrogen by a tungsten filament at 1500° K., which causes a fairly rapid clean-up of dry hydrogen, is entirely prevented by pressures of oxygen or water vapor of an order of magnitude of 10^{-9} mm.[13] A very remarkable phenomenon occurs if a mixture of oxygen and hydrogen at low pressure is admitted to a bulb containing a filament at 1500° K. The oxygen reacts with the filament rapidly to form WO_3, which evaporates at this temperature as fast as formed. The oxygen thus cleans up at a rate proportional to its own pressure and the pressure of oxygen thus falls to half value about every 2 minutes in a bulb of ordinary size. All this occurs exactly as though no hydrogen were present. During this time there is no measurable disappearance of hydrogen. After 10 or 15 minutes the oxygen is nearly all gone and then for 5 or 10 minutes more the gas pressure remains apparently constant and corresponds exactly to that of the hydrogen which was admitted. Then suddenly, when the pressure of oxygen is low enough (10^{-9} mm.), the hydrogen begins to disappear by dissociation and in a few minutes the pressure falls practically to zero. Water vapor has an effect similar to oxygen in preventing the dissociation of hydrogen. At filament temperatures of 1750° K. some of the hydrogen disappears while the oxygen is cleaning up, but the kink in the curve still occurs when the oxygen is gone. Water vapor and oxygen are thus powerful catalytic poisons for the reaction of the hydrogen dissociation.

ARCS IN HYDROGEN AT ATMOSPHERIC PRESSURES

Several years ago in this laboratory studies were made of arcs between tungsten electrodes in various gases. Arcs in hydrogen were remarkable because of the high voltage drop and small cross section. A 10-ampere, direct-current arc between heavy tungsten electrodes about 7 mm. apart in a bulb containing pure hydrogen at atmospheric pressure appeared as a sharply defined, brilliant red line about 0.5 mm. in diameter along which the potential gradient was 150 volts per centimeter, making a power dissipation of 1500 watts per centimeter of length, this being about fifteen times as great as in nitrogen or argon. This abnormal behavior of hydrogen was attributed to the dissociation which carried energy so rapidly out of the arc.

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[13] Langmuir, *Jour. Amer. Chem. Soc., 38,* 2271 (1916); *Trans. Amer. Electrochem. Soc., 29,* 261 (1916); *Gen. Elec. Rev., 25,* 445 (1922).

ARCS IN HYDROGEN AT LOW PRESSURES

In attempting to obtain the Balmer spectrum of hydrogen without contamination by the secondary spectrum, Wood[14] built very long vacuum tubes of moderate bore, in which he passed currents as large as 20 amperes through moist hydrogen at about 0.5 mm. pressure. He observed many remarkable phenomena. Short pieces of tungsten wire projecting into the discharge were heated to incandescence, although a fine thread of glass or a platinum wire in a similar position was apparently not heated by the discharge. On drying the hydrogen with phosphorus pentoxide the secondary spectrum (due to molecular hydrogen) appeared strongly and the Balmer spectrum (due to atomic hydrogen) nearly disappeared. The heating of the tungsten wire was also prevented by drying the hydrogen.

In correspondence with Professor Wood, the writer pointed out that oxygen and water vapor decrease the rate of dissociation of hydrogen in contact with tungsten and must thus also tend to prevent the recombination of hydrogen atoms on a tungsten surface. He also suggested that moisture poisons the catalytic activity of the dry glass surfaces that otherwise converts atomic into molecular hydrogen. Thus with moist hydrogen the tube becomes filled with nearly pure atomic hydrogen and the diffusion of this to the catalytically active tungsten wire causes the heating of the latter. Calculations based on the measured heat of dissociation proved that a pressure of only 0.16 mm. of atomic hydrogen at 500° C. would suffice to maintain a tungsten filament at 2400° K.

These conclusions were confirmed by Wood's observations that the walls of the tube became only slightly heated if the hydrogen was moist, whereas they were strongly heated with dry hydrogen. A tungsten wire was heated red hot even when mounted in a side tube (of 5 mm. diameter) at a distance of 4 cm. from the discharge tube, showing that the hydrogen atoms could diffuse in relatively large quantities out of the discharge.

It occurred to the writer that it should be possible to obtain even higher concentrations of atomic hydrogen by passing powerful electric arcs between tungsten electrodes in hydrogen at atmospheric pressure and this atomic hydrogen could be blown out of the arc by a jet of molecular hydrogen directed across the arc.

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[14] *Proc. Roy. Soc., 102,* 1 (1922); *Phil. Mag. 44,* 538 (1922).

PRELIMINARY EXPERIMENTS WITH FLAMES OF ATOMIC HYDROGEN

To try out the possibility of blowing atomic hydrogen out of an arc, 20-ampere arcs from a constant-current transformer were passed between two tungsten rods 6 mm. in diameter mounted transversely in a horizontal alundum tube (10 cm. diameter) through which a stream of hydrogen flowed. With voltages from 300 to 800, arcs could be maintained with electrode separations up to 2 cm. The magnetic field of the arc caused it to move transversely so that it became fan-shaped. Iron rods 2 or 3 mm. in diameter melted within 1 or 2 seconds when they were held 3 to 5 cm. above the arc.

By directing a jet of hydrogen from a small tube into the arc, the atomic hydrogen could be blown out of the arc and formed an intensely hot flame. To maintain the arc in a stable condition the electrodes were brought close together (1 to 3 mm.), but the arc did not remain entirely between the electrodes, but extended as a fan to a distance of 5 to 8 mm. The flame of atomic hydrogen, however, extended far beyond the arc. At distances of 1 or 2 cm. from the arc molybdenum (m. p. 2900° K.) melted with ease. Near the end of the arc tungsten rods and even sheet tungsten (m. p. 3660° K.) could be melted.

The use of hydrogen under these conditions for melting and welding metals has proved to have many advantages. Iron can be melted without contamination by carbon, oxygen, or nitrogen. Because of the powerful reducing action of the atomic hydrogen, alloys containing chromium, aluminum, silicon, or manganese can be melted without fluxes and without surface oxidation.

TEMPERATURE OF ATOMIC HYDROGEN FLAME COMPARED WITH OTHER FLAMES

Let us suppose we could obtain atomic hydrogen in bulk at atmospheric pressure and room temperature and that we could then let this "burn" to the molecular form in a flame. What would be the temperature of this flame and how would it compare with that of other flames? Taking the heat of reaction (for 2 grams) to be 98,000 calories and taking the specific heat of molecular hydrogen (for 2 grams) to be $6.5 + 0.0009\,T$, we find that the heat of the reaction would be sufficient to heat the hydrogen to 9200° K.

The dissociation of the hydrogen, however, would prevent the temperature from rising to any such high value. If x is the degree of dissociation at the maximum temperature reached, the available heat of recombination is only $(1 - x)$ 98,000.

The heat in calories, Q, needed to raise the temperature of a gram molecule of gas from room temperature (300° K.) to T at constant pressure is[15]

For H (atomic) $Q_1 = 4.97\,T - 1490$
H_2 $Q_2 = 6.50\,T + 0.00045\,T^2 - 1990$
CO or O_2 $Q_3 = 6.50\,T + 0.00050\,T^2 - 2000$
H_2O $Q_4 = 8.81\,T - 0.00095\,T^2 + 7.4 \times 10^{-7}\,T^3 - 2570$
CO_2 $Q_5 = 7.0\,T + 0.00355\,T^2 - 6.2 \times 10^{-7}\,T^3 - 2400$

Thus the temperature that could be reached by the recombination of hydrogen atoms starting from room temperature and atmospheric pressure can be calculated by the equation

$$(1 - x)\,H_0 = 2xQ_1 + (1 - x)\,Q_2 \tag{8}$$

where H_0 is the heat of combination of 2.016 grams of atomic hydrogen at room temperature (98,000 calories). Introducing the values of Q_1 and Q_2 in this equation and solving for x we find

$$x = \frac{100{,}000 - 6.50\,T - 0.00045\,T^2}{97{,}000 + 3.44\,T - 0.00045\,T^2} \tag{9}$$

We can thus plot a curve giving x as a function of T. But the data of Table I enable us to plot another curve of x as a function of T. These two curves intersect at $T = 4030°$ K. and $x = 0.642$. Thus atomic hydrogen at room temperature and atmospheric pressure would heat itself to 4030° K. and the degree of dissociation would then be 0.642.

The temperature of the oxyhydrogen flame can be calculated in an analogous manner, taking into account the dissociation of the water vapor into oxygen and hydrogen and the dissociation of the molecular hydrogen into atomic. This rather laborious calculation shows that the combustion of a mixture of two volumes of hydrogen with one of oxygen at room temperature (300° K.) and atmospheric pressure produces enough heat to raise the reaction products to 3130° K. The reaction is

$$2H_2 + O_2 = 1.652\,H_2O + 0.249\,H_2 + 0.198\,H + 0.174\,O_2 \tag{10}$$

Thus the composition (by volume) of the flame gases at this maximum temperature is water vapor 72.68, molecular hydrogen 10.95, atomic hydrogen 8.71, and molecular oxygen 7.66 per cent. At this temperature the equilibrium constant for the dissociation of hydrogen according to the data of Table I is $K = 0.068$ atmosphere. The corresponding equilibrium constant for the dissociation of water vapor at 3130° K. is[16]

$$K = (H_2)^2\,(O_2)/(H_2O)^2 = 0.00170 \tag{11}$$

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[15] The specific heats for these calculations were taken from a table on p. 80 of Lewis and Randall's "Thermodynamics."

[16] Langmuir, *Jour. Amer. Chem. Soc., 28,* 1357 (1906).

where the parentheses represent pressures in atmospheres. In the flame gases the water vapor is 17.4 per cent dissociated and the hydrogen is 27.4 per cent dissociated.

For the combustion of acetylene with oxygen we may consider the reactions:

$$C_2H_2 + {}^5/_2\, O_2 = 2\, CO_2 + H_2O + 302{,}000 \text{ calories} \qquad \text{I}$$
$$C_2H_2 + {}^3/_2\, O_2 = 2\, CO + H_2O + 166{,}000 \text{ calories} \qquad \text{II}$$
$$C_2H_2 + O_2 = 2\, CO + H_2 + 102{,}600 \text{ calories} \qquad \text{III}$$

In a flame having the proportion of oxygen given in the first reaction the flame gases would contain a relatively large amount of oxygen owing to the dissociation of both the carbon dioxide and the water vapor. For oxy-acetylene welding such strongly oxidizing flames are avoided and the oxygen ratio is cut down nearly as low as that in reaction III.

Let us calculate the temperature and flame composition for this case. The reaction does not go to completion as indicated above in reaction III, but should be written

$$C_2H_2 + O_2 = 2\, CO + n_2 H_2 + n_1 H \qquad (12)$$

where

$$n_2 + {}^1/_2 n_1 = 1 \qquad (13)$$

The heat of the reaction, 102,600 — $(1 - n_2)$ 98,000 calories, must equal the heat content of the reaction products $2Q_3 + n_2Q_2 + n_1Q_1$. From the resulting equation we find

$$n_1 = \frac{108{,}600 - 19.5\, T - 0.00145\, T^2}{48{,}500 + 1.72\, T - 0.000225\, T^2} \qquad (14)$$

The partial pressures of H and H_2 are

$$p_1 = \frac{n_1}{2 + n_1 + n_2} = \frac{n_1}{3 + {}^1/_2\, n_1} \qquad (15)$$

and

$$p_2 = \frac{1 - {}^1/_2\, n_1}{3 + {}^1/_2\, n_1} \qquad (16)$$

so that the equilibrium constant is

$$K = \frac{p_1^2}{p_2} = \frac{n_1^2}{(1 - {}^1/_2\, n_1)\,(3 + {}^1/_2\, n_1)} \qquad (17)$$

At any assumed temperature we can calculate n_1 and thus get K as a function of T. We also get K as a function of T from Table I. The intersection of the two curves gives $T = 3270°$ K.; $n_1 = 0.5676$; $n_2 = 0.7162$.

Thus we conclude that when acetylene burns with an equal volume of oxygen the maximum temperature may rise to 3270° K. and at this temperature the composition of the flame gas is carbon monoxide 60.9 per cent, molecular hydrogen 21.8 per cent, and atomic hydrogen 17.3 per cent by volume.

There is another factor which tends greatly to increase the temperature of the atomic hydrogen flame even above the calculated value of 4030° K. The atomic hydrogen, instead of being originally at room temperature, is already at a high temperature at the moment of its escape from the arc. The conditions are analogous to those in an oxyhydrogen flame in which both gases are preheated. Thus the upper limit of temperature is fixed only by the degree of dissociation of the hydrogen and the rate at which heat is lost by radiation or contact with bodies of lower temperature.

RATE OF SURFACE HEATING BY FLAMES

Although the high temperature of the atomic hydrogen flame is of great importance when it is desired to melt substances of very high melting point such as tungsten, a factor of even greater importance in ordinary welding operations is the rapidity with which heat can be delivered to a surface per unit area.

TABLE II

Rate of Surface Heating Produced by Various Flames

					Watts/sq. cm.
(1)	Ordinary Bunsen burner (gas-air) at tip of inner cone. Flame 15 cm. high, cone 4.5 cm. high				51
(2)	Ordinary blast lamp (gas-air), 14 cm. from burner tip in flame 25 cm. long, nozzle 0.60 cm. diameter				57
(3)	Same at 19 cm. from burner tip (hottest part)				73
(4)	Ordinary blast lamp (hydrogen-air), 13 cm. from burner tip				100
(5)	Blast lamp for quartz blowing (gas-oxygen) 2.5 cm. from burner tip				450
(6)	Same with hydrogen-oxygen				520
(7)	Acetylene welding torch, adjusted for maximum effect (several different tips gave about the same result)				670
(8)	Atomic hydrogen flames:				
		Amperes	Volts	Mm. from tips	
		20	100	3	580
				5	640
				7	400
		40	75	3	1000
				5	1140
				7	900
				10	620
		60	65	5	1300
				7	1100
				10	850
				15	500
				20	330
				30	190
				40	130
				50	95

In order to determine this rate of surface heating for various kinds of flames, the device shown in Figure 2 was constructed. It consists essentially of a short rod of tungsten, *A*, so arranged that heat from the flame can be applied only to the circular surface forming its upper end, while its lower end is in good thermal contact with a large mass of copper, *B*, which removes the heat from the tungsten rod as fast as it is delivered by the flame. To prevent the flame from striking the sides of the rod, a water-cooled circular plate or guard ring of copper, *C*, is used. To obtain good thermal contact between the tungsten rod and the copper, the mass of copper *B* was made by casting it around the tungsten rod which had previously been covered with copper by heating with copper in an atmosphere of hydrogen. The tungsten rod had a diameter of 0.77 cm. and the portion extending out of the copper mass had a length of about 0.8 cm. The hole in the copper plate was 0.95 cm. in diameter. The weight of the copper block *B* was 8100 grams and the diameter of its cylindrical part was 10 cm.

The temperature of the copper block was measured at half-minute intervals by means of a mercury thermometer placed in a hole which had a diameter only slightly larger than the thermometer and into which oil had been introduced to make better thermal contact between the thermometer and copper.

When the atomic hydrogen or other flame was directed against the tungsten tip the rate of temperature rise of the copper block gave a measure of the rate of surface heating. The flame was applied for a definite time which ranged from 2 to 5 minutes, during which time the temperature rose 40° to 80° C. After the flame was removed the thermometer readings continued to rise for a couple of minutes because of the time needed for the heat to become uniformly distributed throughout the copper block. Readings were continued for several minutes more in order to determine the rate of cooling so that correction could be made for the slight loss of

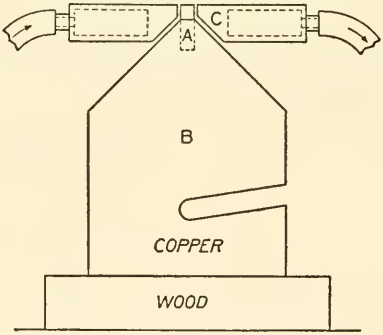

Fig. 2.—Apparatus for Measuring Rate of Surface Heating Produced by Flames.

heat that occurred before the maximum temperature was reached. This correction rarely amounted to more than 5 per cent.

The rate of surface heating in watts per square centimeter was then calculated from the temperature rise, the time of application of the flame, the area of the end of the tungsten tip (0.466 sq. cm.), the mass of copper and its specific heat (0.394 watt second per gram per degree). A summary of the results is given in Table II. Except where specifically noted, the conditions for the use of each flame were chosen to give the greatest possible rate of surface heating.

The rate at which heat is delivered to a tungsten surface by the atomic hydrogen flame produced by a 60-ampere arc (1330 watts per sq. cm.) is thus twenty-six times as great as that from a Bunsen burner flame and about double that from the flame produced by the ordinary oxy-acetylene welding torch.

According to the Stefan-Boltzmann law the heat radiated from a body at high temperature is

$$W_R = 5.7\,E\left(\frac{T}{1000}\right)^4 \text{ watts per sq. cm.} \qquad (18)$$

where E is the emissivity of the body ($E = 1$ for a black body).

If a Bunsen burner flame delivers 51 watts per sq: cm. to the whole surface of a black body, it would thus heat it to 1730° K. If heat is applied by the flame to one side of a plate-shaped body and the heat is radiated from both sides, the temperature would be 1450° K. The fact that the Bunsen flame does not heat bodies so hot as this indicates that the rate of surface heating decreases as the temperature of the body increases. The heat reaches the surface from such a flame by conduction through a relatively stationary film of gas. The decrease in the temperature gradient when the body becomes hot would explain the lower rate of surface heating. With

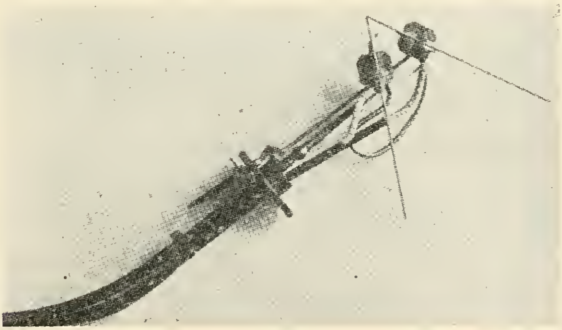

Fig. 3.—One Form of Atomic Hydrogen Welding Torch.

1330 watts per sq. cm. delivered by the atomic hydrogen flame, the temperature of a black body would rise to 3900° K. The power radiated from tungsten at its melting point is 395 watts per sq. cm., and 1330 watts per sq. cm. should heat tungsten to about 5300° K. Although tungsten wires and even sheet metal can be melted and welded by the atomic hydrogen flame, it does not occur so rapidly as the foregoing figures would lead us to expect.

At such high temperatures, however, the rate of surface heating by an atomic hydrogen flame must decrease because of the fact that the hydrogen remains partly dissociated so that the recombination is not complete. With surface temperatures below 2000° K., however, this factor would be negligible. It is probable that the rate of surface heating would be dependent not so much on the temperature gradient in the surface film of gas as on the rate of diffusion of atomic hydrogen through this film. Thus we may expect the rate of delivery of energy to a metal surface to remain nearly constant until the surface reaches a temperature of at least 2000° K.

To test this conclusion and also to find out whether different metals are heated at different rates, another device like that shown in Figure 2 was constructed, but the tip which was heated was of copper instead of tungsten, being made by turning down a large block of copper. When energy is delivered at the rate of 1000 watts per sq. cm. the temperature gradient in the tungsten tip is about 1100° K. per cm., while with a copper tip it is 260° K. per cm. Thus the surface of the tungsten tip was probably at a temperature of at least 1400° K. while the copper surface was not over 600 °K. The observed rates of surface heating with the copper and tungsten tips were, however, not measurably different. This seems to indicate that up to 1400° K. the temperature of the surface does not affect the rate of heating and also that copper and tungsten are equally effective in causing recombination of hydrogen atoms on their surfaces.

TOTAL HEAT DELIVERED TO SURFACES

The foregoing method measures the intensity of surface heating in watts per square centimeter. It was of interest to determine what fraction of the total energy in an arc or a flame could be delivered to a large flat surface against which the flame was directed. For this purpose a cylinder of copper 10.5 cm. in diameter and 9.8 cm. long was used, which weighed 7950 grams. The flame was directed against one of the flat polished ends, and the rate of temperature rise was measured as before.

An atomic hydrogen flame was produced by a 60-ampere a. c. arc using a torch like that shown in Figure 3. The voltage across the electrodes was 70 volts. A wattmeter showed that the power consumption in the arc was 3510 watts, which gives a power factor of 0.84. The electrodes were tungsten rods 3.2 mm. in diameter which made an angle of 55 degrees with one another. The rate of flow of hydrogen which bathed the electrodes was 14.2 liters per minute (30 cubic feet per hour). From the temperature rise of the copper block the heat delivered to the surface was found to correspond to 3100 watts when the electrode tips were 3 to 5 mm. from the copper surface. This decreased to 2800 watts at 13 mm., 2500 at 25 mm., and 2200 at 35 mm. With the arc turned off but the molecular hydrogen burning in the air, the rate of heating corresponded to 250 watts with the electrodes 6 mm. from the surface. Subtracting this energy delivered by the combustion of the hydrogen in the air, we find that the energy carried to the metal by the atomic hydrogen ranged from 2850 to 1950 watts. Thus with the electrodes 3 mm. from the metal 82 per cent of the power input into the arc was delivered to the copper surface. This efficiency became 78 per cent at 6 mm., 71 at 13 mm., 65 at 25 mm., and 55 per cent at 35 mm. The energy corresponding to the complete combustion of 14.2 liters of hydrogen per minute is 2360 watts. Actually, only 250 watts or 11 per cent of this reaches the copper. The total energy of the arc and the flame of molecular hydrogen is 5870 watts, of which 3100 watts or 53 per cent is delivered to the copper.

An oxy-acetylene flame from a standard welding torch consuming 30.6 liters of oxygen per minute (64.8 cubic feet per hour) and 28.6 liters of acetylene per minute (60.6 cubic feet per hour) delivered energy at the rate of 4400 watts to the copper surface. A smaller torch consuming 13.7 liters of oxygen per minute and 13.0 of acetylene (29.0 and 27.5 cubic feet per hour, respectively) gave energy to the copper at the rate of 3900 watts. If we take the heat of combustion of the acetylene to be 302,000 calories corresponding to complete oxidation according to reaction I, the efficiency of the heat delivery by these flames is 17.6 per cent with the larger torch and 34.2 with the smaller. The energy delivered is, however, 52 and 101 per cent, respectively, of the heat energy generated if the combustion proceeded only as far as indicated by reaction III.

The data in Table II and the foregoing results show that the intense heat of the atomic hydrogen flame extends a considerable distance beyond the arc between the electrodes. Some measurements were also made of the length of time required to melt the end of rods 6.3 mm. in diameter (¼ inch) of Armco iron which were held in the flame at different distances from the electrode tips, the axis of the rods being perpendicular to the direction of motion of the flame gases. The rods were at room temperature when introduced into the flame. Table III gives the time in seconds before fusion at the end of the rod occurred.

Every refractory material which has been tried, except carbon, can be melted with comparative ease by the atomic hydrogen flame. Many substances vaporize very rapidly. The flame from a 60-ampere arc was directed against a large piece of calcium oxide. After considerable shrinkage and cracking a surface of several square centimeters can be maintained in a molten condition (m. p. of CaO, 2850° K.),[17] but evaporation occurs with remarkable rapidity. The flame becomes very brilliant and of a red color, and a spectroscope shows many hundreds of lines extending over nearly the whole spectrum. An optical pyrometer with a red screen ($\gamma = 0.66\ \mu$) sighted on the fused lime when at its highest temperature showed that the luminous intensity corresponded to that of a black body at 3500° K. A large fraction of this light was undoubtedly emitted by the gas.

TABLE III

TIME REQUIRED TO MELT ENDS OF 6.3-MM. IRON RODS IN FLAME FROM 60-AMPERE ARC

Distance from Electrodes		Time
Mm.	*Inches*	*Seconds*
6.3	¼	4
9.5	⅜	7
13	½	8
19	¾	14
25	1	18
38	1½	27
51	2	36
64	2½	80
76	3	240

ACTION OF ATOMIC HYDROGEN ON VARIOUS REFRACTORY SUBSTANCES

Pure magnesium oxide (m. p. 3070° K.) melts with much greater difficulty. When it reaches high temperatures the arc shows a strong tendency to short-circuit on to the heated mass and rapid evaporation occurs where the arc leaves and enters the oxide. The end of a rod of oxide 4 × 7 mm. in cross section was heated just to fusion for 1.5 minutes and its weight decreased from 1.74 to 1.01 grams. The observed black-body temperature just at fusion was 3070° K., but the apparent temperature could be raised to 3200° K. Relatively little light was emitted by the flame gases.

Pure thorium oxide, ThO_2 (m. p. > 3070° K.), when just fused gave a black-body temperature of 3360° K., but the apparent temperature could be raised to 3700° K. at the points where the arc short-circuited on to the hot oxide. Evaporation was very rapid under these conditions.

With none of these oxides, or with alumina, was there any direct indication of reduction of the oxide to metal. A water-cooled, polished copper surface held in the flame just over the heated oxide rapidly became coated with oxide, but no metal was observed. It may well be, however, that the apparent volatility of the oxides is in large part due to reduction of the oxides and evaporation of the resultant metal, but as the temperature of the flame gas is lowered by cooling, the metal vapor reacts with the water vapor or oxygen derived from the original oxide.

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[17] These melting points are taken from the International Critical Tables.

Quartz glass seems peculiarly difficult to fuse. At least, with the most intense heat of the arc it retains a very considerable viscosity. For example, when the atomic hydrogen flame is directed against the central part of a thin piece of quartz glass about 3 mm. thick, it does not seem possible to *melt* a hole through the sheet of glass. Right under the arc, however, the silica evaporates rapidly so that after perhaps half a minute, but without any further increase in temperature, the glass becomes so thin that a hole forms. The hottest part remains clear and the surface clean, but this region is surrounded by a ring where the surface is covered by a fairly thick film of silicon or lower silicon oxides. On cooling the sample by removal from the flame, this ring appears black or dark brown with a peculiar luster, but in the flame the central part appears dark because of its low emissivity while the surrounding ring is bright. Pyrometer readings of the sample when strongly heated give black-body temperatures of 2530° K. for the central part and 2690° K. for the inner edge of the ring.

The inability to get the silica in a more fluid condition is due partly to its inherently high viscosity. Cooling by rapid evaporation, and perhaps failure of the quartz to catalyze the reaction involving the recombination of the hydrogen atoms, probably limit the temperature to which the quartz can be heated.

EVAPORATION OF METALS

Pieces of various metals weighing 3 to 6 grams were placed upon cupels made from pure magnesium oxide, and were heated as strongly as possible by an atomic hydrogen flame from a 60-ampere arc. Cracks which formed in the cupels, through which molten metal could escape, were repaired by fusing small amounts of lime into the surface. Of course, a flame directed against the surface of a liquid cannot raise the temperature of the liquid to the boiling point, for cooling by evaporation will hold the temperature below this point. Thus, a Bunsen burner flame playing on the surface of water in a small dish heats the water to only about 85° C. Table IV gives maximum temperatures to which various metals could be heated by the atomic hydrogen flame.

These temperatures were calculated from the pyrometer readings by

TABLE IV

Maximum Temperatures of Metals Heated by Atomic Hydrogen Flame

Metal	$T_{\text{Max.}}$	$T_{\text{b.p.}}$	Radiation	Evaporation	Rate of Evaporation	Emissivity
	° *K.*	° *K.*	*Watts per sq. cm.*		*G./cm./cm./sec.*	
Ni	2870	3650	140	60	0.0095	0.36
Cu	2840	3110	37	300	0.058	0.11
Ag	2660	2740	20	330	0.125	0.07

means of the emissivities given in the last column. The boiling points in the third column were obtained from measurements of the rate of evaporation from these metals in vacuum.[18]

The rate of radiation of energy from the surface of the metal in watts per square centimeter is given in the fourth column while the heat energy corresponding to the cooling of the metal by its evaporation in the flame is given in the fifth column. The observed rate of loss of weight in grams per square centimeter per second is in the sixth column. It is clear that the cooling by evaporation limits the temperature to which molten metals can be heated except in the case of such difficult volatile metals as molybdenum and tungsten.

APPLICATION OF ATOMIC HYDROGEN FLAMES TO WELDING OF METALS

The high temperature of this flame, together with its powerful chemical reducing action and the avoidance of gases containing oxygen and nitrogen, render it particularly useful for welding, not only for iron and its alloys, but for such metals and alloys as contain aluminum, magnesium, chromium, manganese, etc.

Since a general account of these applications has already been published,[19] only a brief summary will be given here. The technical development of these processes is largely the work of R. A. Weinman.

Figure 3 illustrates one of the later forms of torch used for welding. Two tungsten rods, as electrodes, are held at a definite angle to one another by easily adjustable clamps, and a jet of hydrogen is directed from a small nozzle along each of these rods near its end. The hydrogen thus bathes the heated parts of the electrodes and forms a gentle blast of gas which passes through the arc between the electrode tips, and blows the atomic hydrogen away from the electrodes so that these are not unduly heated. Other torches have been built suitable for automatic welding using machine feed.

[18] These data will soon be published by H. A. Jones and the writer in *Phys. Rev.*

[19] Weinman and Langmuir, *Gen. Elec. Rev.*, *29*, 160 (1926).

The electrodes are ordinarily separated 3 or 4 mm. and the arc assumes a fan shape extending 6 to 10 mm. from the electrodes. Alternating current is generally used.

Figure 4 illustrates some welds made by the use of this method. At the center is shown a weld between two pieces of ⅛-inch sheet steel (low carbon). The weld is of very high strength and ductility, as is shown by its ability to stand the three mechanical embossing operations to which it was subsequently subjected.

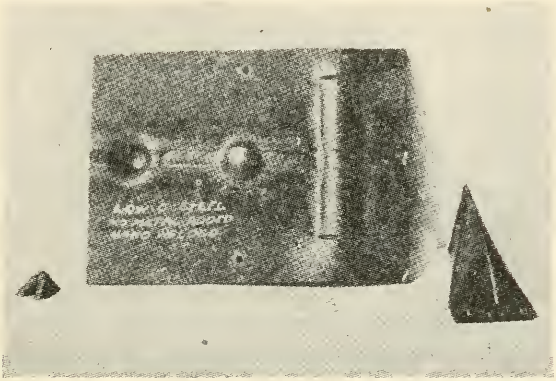

Fig. 4.—Welds of Low Carbon Steel Made with Atomic Hydrogen Torch.
Left—Welded sheet $\frac{1}{16}$ inch thick, folded twice.
Center—Weld ⅛ inch thick, tested by embossing.
Right—Tube made by welding sheet $\frac{1}{32}$ inch thick, subsequently subjected to tests.

The small sample to the left illustrates a particularly severe test for ductility. The $^{1}/_{16}$-inch sheet metal (low carbon steel) after being welded, as in the case just discussed, was folded double along the line of the weld and then folded double a second time at right angles to the first fold. The sample shows a piece cut from the corner of this double fold. The metal shows no signs of cracking.

The third sample at the right illustrates a cylindrical tube made from low carbon steel sheet metal $^{1}/_{32}$ inch thick.

After being welded the tube was flattened at its ends in two directions at right angles to each other. The weld showed no signs of failure.

Chapter Nine

THE DISSOCIATION OF HYDROGEN INTO ATOMS*

PART ONE

Some early measurements [1] of the heat loss by convection from heated tungsten wires in hydrogen showed that the loss increased at an abnormally high rate when extremely high temperatures were reached.

A little later [2] a series of measurements on the heat convection from various kinds of wires in different gases led to a general theory of convection from hot bodies, which makes possible the approximate calculation of heat losses from a wire at any temperature in any gas which behaves normally.

With hydrogen, the theory led to results in close agreement with the experiments, up to temperatures of about 2300° K. Above this, however, the observed heat loss increased rapidly until at 3300° K., it was over four times the calculated value.

This fact suggested that the hydrogen was partly dissociated into atoms at these high temperatures.

In a subsequent paper,[3] the theory of heat conduction in a dissociating gas was developed to apply to this case.[4] It was shown that the power re-

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* In collaboration with G. M. J. Mackay.

[1] Langmuir, *Trans. Am. Electrochem. Soc., 20,* 225 (1911).

[2] Langmuir, *Phy. Rev., 34,* 401 (1912).

[3] Langmuir, *Jour. Amer. Chem. Soc., 34,* 860 (1912).

[4] At the time of publication of the above mentioned paper, I was unaware that Nernst had previously (Boltzmann, *Festschrift, 1904,* p. 904) developed a quantitative theory of the heat conduction in a dissociating gas, and had shown that the heat conductivity of nitrogen peroxide, determined by Magnanini, agreed well with that calculated by his equations from the known degree of dissociation of this substance. Nernst showed that the effect of the dissociation is to increase the heat conductivity of a gas by an amount equal to

$$\mathrm{D}q\frac{dc}{d\mathrm{T}}.$$

He does not, however, show that this leads to the very simple and useful form of equation developed by the writer, namely,

$$\mathrm{W_D} = \mathrm{SD}q\,(\mathrm{C} - \mathrm{C'}).$$

Nernst points out that the heat conductivity of gases may be used not only to detect dissociation qualitatively, as R. Goldschmidt (Thesis, Brussels, 1901) had shown, but in some cases to determine the degree of dissociation quantitatively. (I. Langmuir.)

quired to heat the wire could be expressed as the sum of two terms, thus:

$$W = W_C + W_D \qquad (1)$$

Here W is the total power (in watts per centimeter) required to maintain the wire at a given temperature T_2.

W_C represents the part which is carried by ordinary heat conduction and follows the usual laws of heat convection, namely:[5]

$$W_C = S\int_{T_1}^{T_2} k\,dT = S(\varphi_2 - \varphi_1) \qquad (2)$$

S is called the shape factor and depends on the diameter of the wire and the nature of the gas, but is independent of the temperature of the wire. k is the coefficient of heat conductivity of the gas, W_D represents that part of the heat loss which is dependent on the dissociation of the gas. It was shown that W_D could be expressed thus:

$$W_D = SDq_1C_1 \qquad (3)$$

where S is the shape factor, D is the diffusion coefficient of hydrogen atoms through molecular hydrogen, q_1 is the heat of formation of hydrogen molecules from 1 g. of hydrogen atoms, and C_1 is the concentration of hydrogen atoms (grams per cc.) in the gas immediately in contact with the hot wire.

The experiments gave W directly (after subtracting the heat radiated from the hot wire). The value of W_C could be calculated by (2) and thus equation (1) led to a determination of W_D. By substituting in (3) the values of S and W_D, the product Dq_1C_1 was obtained from the results of the experiments.

It was then necessary to estimate the approximate value of D. This was done by guessing the probable free path of hydrogen atoms through hydrogen molecules by analogy with other gases and by then substituting this value in an equation, derived from the kinetic theory, which expresses the diffusion coefficient in terms of the normal free path.

Having thus chosen D and dividing this into the known value of Dq_1c_1, the product q_1c_1 was found. Van't Hoff's equation gives a relation between q_1 and the temperature coefficient of c_1. Since q_1 is nearly independent of the temperature, the temperature coefficient of c_1 must be practically equal to that of q_1c_1, so that in this way q_1 could be found. From this, the value c_1 and the degree of dissociation was then calculated.

The degree of dissociation of hydrogen into atoms (at atmospheric pressure) was thus calculated to be 1.2% at 2300° K., and 44% at 3100° K., and 84% at 3500° K. The heat of formation of the molecules from the atoms was given at 130,000 calories (for 2 g. of hydrogen).

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[5] *Phys. Rev., l. c.*

These results seemed to conflict seriously with the measurements of the specific heat of hydrogen obtained by the explosion method. Pier[6] had concluded from his experiments that the mean specific heat of hydrogen from room temperature up to 2500° K. could be represented by the equation

$$C_v = 4.70 + 0.00045t$$

On the other hand, Bjerrum[7] found that the specific heat of water vapor was abnormally large at temperatures above 2000° K.

The method adopted by Bjerrum was one in which it was not possible to distinguish between variations in the specific heat of water vapor and of hydrogen. An increase of perhaps 10–20% in the specific heat of hydrogen at 3000° would, therefore, be quite consistent with Bjerrum's experiments.

A dissociation as high at 44% at 3100° K. would, however, lead to an apparent specific heat of H_2 two or three times greater than the usually accepted value.

One explanation of this discrepancy might be that the velocity of the hydrogen dissociation is so small that during the short time of an explosion, equilibrium was not reached, whereas in the other experiments, the catalytic action of the hot tungsten wire caused the dissociation to approach the equilibrium more closely.

It seems, however, improbable that the velocity of the reaction would be so slow at temperatures as high as 3100° K. Bjerrum's experiments, therefore, seem to indicate that the degree of dissociation is considerably less than the values obtained by the methods described above.

If we examine the chain of reasoning by which the results were obtained we see that there is one extremely weak link, namely, the method by which the diffusion coefficient D was obtained.

It is true that this method would give a fair degree of accuracy if applied to almost any pair of ordinary gases at ordinary temperatures, but a good deal of uncertainty arises when it is applied to a dissociating gas. In fact, under such conditions, the diffusion coefficient might be very much greater than that calculated in the usual way. An example of such a case is already known in the abnormally great mobility of the hydrogen and hydroxyl ions in aqueous solutions. A larger value for the diffusion coefficient would lead to lower values for the dissociation and might thus

[6] *Z. Elektrochem.*, *15*, 536 (1900).

[7] *Z. physik. Chem.*, *79*, 513 (1912).

remove the discrepancy between the previous calculations and Bjerrum's results.

QUALITATIVE EVIDENCE FOR THE DISSOCIATION OF H_2

H. von Wartenberg,[8] after pointing out the discrepancy between the former calculations and the results of the explosion method criticises the heat conductivity method as follows:

"Die Fehlerquellen der Methode sind zu gross, als dass man die Zahlen auch nur als annähernd richtig betrachten könnte, wenn auch eine geringe Dissociation des H_2 von etwa 2100° nicht als ausgeschlossen erscheint. Sichere Zahlen wird wohl nur die Explosionsmethode geben können."

As far as accurate quantitative determinations of the degree of dissociation of most complex gases are concerned, we feel that von Wartenberg's preference for the explosion method is justified, but for qualitative evidence of dissociation, especially of elementary gases, we consider that the heat conductivity method has great advantages over the explosion method. The fact that mixtures of gases must be employed in the latter method, so complicates the phenomena that there is considerable uncertainty in the interpretation of results. Furthermore, it will be shown that the conductivity method, in some cases, is very much more sensitive that the explosion method.

The qualitative evidence of dissociation of hydrogen obtained by the heat conduction method and already published, may be briefly summarized as follows:

1. The heat loss from tungsten wires (or platinum wires up to 1750°) in nitrogen, mercury vapor, argon, and carbon monoxide varies with the temperature accurately, as expressed by equation (2).
2. The heat loss in hydrogen follows accurately the same law up to about 1900° K. and then rapidly increases, until at 3500° K. it is over four times its calculated value.
3. No secondary electrical effects which might cause a similar increase can be detected.
4. At lower pressures the heat loss from tungsten wires in hydrogen becomes actually *greater* than at atmospheric pressure. This does not occur with other gases.

The evidence of dissociation is, however, not at all limited to the abnormal heat conductivity.

A large amount of evidence of a chemical nature has gradually accumulated in this laboratory, which proves, beyond doubt, that hydrogen at low pressures, upon coming in contact with a heated metallic wire, is chemically activated and can, under proper conditions, retain its activity several days. A very brief review of this evidence will be of interest.

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[8] *Z. Elektrochem., 19,* 901 (1913).

1. It has been shown[9] that when a wire of tungsten, platinum or palladium is heated to a temperature above 1300° K. in hydrogen at very low pressure (0.001 to 0.020 mm.), the hydrogen slowly disappears. There is a distinct fatigue effect, but the substitution of a new section of wire does not restore the action. The hydrogen is not absorbed by the wire, but is deposited on the glass, especially where this is cooled by liquid air. If the cooled portions are heated, ordinary hydrogen is liberated which will not recondense on replacing liquid air. The hydrogen may deposit on cooled glass surface, even in tubing at a considerable distance from the bulb. This hydrogen has remarkable chemical activity and will react with oxygen and phosphorus at room temperature. These effects are not due to the catalytic effect of finely divided metal deposits. The active hydrogen is not affected by an electrostatic field and therefore does not consist of hydrogen ions.

2. The active hydrogen thus produced can diffuse through long tubes (at low pressures) and can then dissolve in platinum (at 50°) and cause a marked increase in its electrical resistance and corresponding decrease in its temperature coefficient. Ordinary hydrogen, under similar conditions, will not do this. These effects have been described in some detail by Freeman.[10]

3. It has been found that tungstic oxide, WO_3, platinum oxide, PtO_2,[11] and many other substances, placed in a bulb containing a tungsten filament and hydrogen at very low pressures, rapidly become chemically reduced when the filament is heated to a temperature exceeding about 1700° K. although otherwise they are not acted on by hydrogen.

Many of these phenomena have been studied quantitatively in some detail, and the results seem consistently to be in accord with the theory that a portion of the hydrogen which comes into contact with the hot wire is dissociated into atoms. These, perhaps because of strong unsaturated chemical affinity, tend to adhere to glass surfaces even at room temperature. Some, however, leave the glass and wander further. Gradually the glass surfaces become charged with hydrogen atoms to such an extent that any fresh atoms striking the surface, combine, even at liquid air temperatures, with those already present. In case the atoms strike a metal surface such as platinum, they dissolve in it up to a considerable concentration.

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[9] "A Chemically Active Modification of Hydrogen," Langmuir, *Jour. Amer. Chem. Soc.*, *34*, 1310 (1912).

[10] *Jour. Amer. Chem. Soc.*, *35*, 927 (1913).

[11] Formed and deposited on the bulb by heating Pt at very high temperature in O_2 at low pressure or by passing a glow discharge between Pt electrodes in O_2 at low pressure.

The foregoing results afford satisfactory proof that hydrogen, particularly at low pressures, is readily dissociated into atoms by metallic wires at very high temperatures.

There is, however, good reason to suspect that the actual values for the degree of dissociation previously given are considerably too high. The cause of this was thought to be an incorrect assumption as to the diffusion coefficient of hydrogen atoms through molecular hydrogen.

The remainder of the present paper deals with the results obtained by two methods which lead to more or less quantitative data on the dissociation, without necessitating any assumptions as to the magnitude of the diffusion coefficient.

The first method is based on measurements of the total heat losses from tungsten wires at a series of different pressures, ranging from 10 mm. up to atmospheric pressure. If the previous results were correct, that is, that hydrogen is 44% dissociated at atmospheric pressure and 3100° K., then, at a pressure of 10 mm., the dissociation should be 96.5%. A further rise in temperature could then only slightly increase the degree of dissociation, for it is already close to the limit of 100%. We see, then, from equation (3), that the heat loss under these conditions would have only a very small temperature coefficient. It was hoped, at the outset of these experiments, that the actual degree of dissociation could be determined from the decrease in the temperature coefficient of W_D as the pressure was progressively lowered.

The experiments to be described have shown, however, that even at 10 mm. pressure the temperature coefficient of W_D is practically as great as at atmospheric pressure, showing that even at these low pressures the hydrogen around the wire is not nearly completely dissociated. These experiments, however, give an upper limit to the degree of dissociation.

In the second method, measurements were made at very much lower pressures, from 0.01 mm. up to 0.2. At the lowest pressures, the conditions should become very simple, for the molecules travel in straight lines directly from filament to bulb. Under such conditions, the hydrogen atoms produced practically never return to the filament without having struck the bulb many times and having had ample opportunity of recombining. The filament is, therefore, struck only by hydrogen molecules, and from the formula

$$m = \sqrt{\frac{M}{2\pi RT}}p \qquad (5)$$[12]

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[12] Here m is the rate (in grams per sq. cm. per second), at which the hydrogen comes into contact with the filament. M is the molecular weight of H_2 (*i.e.*, 2), T is the temperature of the bulb, and p is the pressure of the hydrogen in the bulb. The derivation of this equation has been given in a previous paper (*Phys. Rev. N. S.*, *2*, 329 (1913)) and *Physik. Z.*, *14*, 1273 (1913).

the rate at which the hydrogen molecules reach the surface may be calculated. If, then, the heat loss be determined by experiment, the energy carried away by each molecule can be calculated. If, by heating the filament to very high temperatures, a condition could be reached in which every hydrogen molecule which strikes the filament becomes dissociated, then those experiments would lead to a direct determination of the heat of formation (heat absorbed by dissociation) of hydrogen molecules. In the absence of definite evidence that the dissociation is complete, the method gives at least a lower limit for the heat of formation.

EXPERIMENTS ON THE HEAT LOSSES FROM TUNGSTEN WIRES IN HYDROGEN

1. *Higher Pressures.*—In the experiments upon which the former calculations of the dissociation were based, the measurements of heat loss were made from short pieces of tungsten wire mounted vertically in a large glass tube open at the lower end, through which a fairly rapid stream of hydrogen passed. The temperature in most cases was determined from the resistance. The relation between resistance and temperature was, however, found by measurement of the intrinsic brilliancy of pieces of the same wire mounted in exhausted bulbs.

In the present experiments, it was desired to employ a series of different pressures of hydrogen around the filament, and furthermore, to avoid injury to the wire by impurities in the hydrogen.

The method adopted was therefore to mount single loop filaments of pure tungsten wire in large heater lamp bulbs (cylindrical bulbs about 25 cm. long and 7 cm. diameter) which were filled with pure, dry hydrogen at various pressures. These were then set up on the photometer bench and a series of simultaneous measurements of candle power, current and voltage were made. The color of the light emitted was also accurately matched against that from a standard lamp viewed through a special blue glass.[13]

Before filling the bulbs with hydrogen, they were exhausted to 0.1 micron pressure for an hour while heated to 360°, and the filaments were heated to a high temperature to drive off gases. The hydrogen was prepared electrolytically and was freed from oxygen and water vapor with extreme care.

Thirty lamps were made up for these experiments. Fifteen of these were filled with hydrogen at the following pressures: 1, 10, 25, 50, 100, 200 and 750 mm. Six were exhausted to a good vacuum in order to determine the amount of energy radiated. The remainder were filled with pure nitrogen at various pressures, to compare the heat loss in this gas with that in hydrogen.

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[13] This method has proved extremely accurate and serviceable as a means of comparing the temperatures of tungsten filaments. It is described in some detail by Langmuir and Orange, *Proc. Amer. Inst. Elect. Eng., 32,* 1895 (1913).

The wire used in all lamps was 0.00706 cm. diameter. In every case it was welded to nickel leads with tungsten or molybdenum tips. The length of wire used in the hydrogen lamps ranged from 5 to 9 cm. and in the vacuum and nitrogen lamps, from 6 to 12 cm. It was necessary to use rather short lengths in hydrogen in order to be able to heat the wire to the melting point without using voltages over 200 volts.

Temperature Measurements.—The temperatures were determined, as has been usual in this laboratory, by the relation

$$T = \frac{11230}{7.029 - \log H} \qquad (6)$$

where H is the intrinsic brilliancy of the filament in international candle power per sq. cm. of projected area. On this scale the melting point of tungsten proves to be 3540° K. (by direct experiment). This value we consider to be more probable than the lower values usually given.

The temperatures were also determined by two auxiliary methods: by measurement of the resistance and by matching the color of the emitted light against that of a standard provided with a blue screen. In both these methods, however, the primary standard of temperature was the one given above, based on the intrinsic brilliancy of the filament.

It was found in nearly all experiments that the three methods gave concordant results. The presence of hydrogen or nitrogen did not change either the resistance or the color of the light emitted from a filament set up at a given intrinsic brilliancy. Discordant results were obtained only in the experiments in vacuum or low pressures of gas after the filament had been heated some time above 3200° K. and had evaporated so that the bulb had blackened and the diameter of wire had changed.

In order to avoid errors in temperature due to the cooling effect of the leads, the candle power was usually determined through a slit, one or two centimeters wide, placed horizontally in front of the lamp. In this way, the intrinsic brilliancy can be determined with accuracy.

At temperatures below 1800° K., the candle power determinations were too inaccurate to be suitable for temperature measurements. The temperatures were, therefore, found in these cases from the resistance, proper correction being made for the cooling effects of the leads.

Before making measurements on the lamps, they were thoroughly aged by running them for 24 hours with the filaments at a temperature of about 2400° K. With the hydrogen and nitrogen of the purity used in these experiments, this treatment produced no perceptible injury of the filament. During the first few hours of aging, the filament, even in vacuum lamps, undergoes slight changes in resistance, and it was with this object, as well as to test the purity of the gases, that the lamps were subjected to the aging process.

The lamps were then set up on the photometer one by one, and measurements of current, voltage, candle power and color were made. About 30 to 50 sets of readings were taken with each lamp, raising the voltage usually in steps of 2.5 to 5 volts at a time. The temperature was thus gradually raised from 800° K., up to about 2900°. Then a series of points was taken at descending temperatures and finally the temperatures were raised to temperatures of 3000° and more, frequently repeating some of the measurements at lower temperatures to see if the filament had undergone any change. The readings up to 3000° K. could be taken without haste, as the filament undergoes only relatively slow changes below this temperature. Above this temperature the readings were taken as rapidly as possible, and at wider intervals (usually 10 volts). These precautions were especially necessary with the lamps containing less than 100 mm. of gas. In those containing nearly atmospheric pressure of either hydrogen or nitrogen, there was never any perceptible darkening of the bulb, and the loss of material from the filament was extremely small, even when the temperature was raised several times very close to the melting point of the filament.

From the data thus obtained, the power consumption (in watts per centimeter of length), the temperature, and the resistance (per centimeter) were determined. The watts per cm. were plotted on semi-logarithmic paper against temperature and smooth curves drawn through the points.

Most of the points fitted very closely (within 1 or 2%) with the smoothed curves, and it was only rarely, at very low and at very high temperatures, that deviations as great as 5% were observed.

The results of these experiments are summarized in Table I. The energy *radiated* from the filament per second (in watts per centimeter of length) is given in the second column under the heading W_R. This was obtained from the lamps with well exhausted bulbs. The resistance (in ohms per centimeter) of the filament is given in the third column headed R. These values represent the averages of all the lamps. There was no appreciable difference in R for the gas filled and the vacuum lamps. The next six columns contain the data obtained from the bulbs containing hydrogen. The figures give directly the energy carried from the filament by the gas, the values tabulated being obtained by subtracting W_R from the observed total power consumption (in watts per cm.).

The last five columns contain similar data obtained from the nitrogen filled lamps.

Simple observation of these figures shows the very striking difference

TABLE I

Temp. ° K.	W*R*.	R.	Watts per cm. carried by hydrogen. 750 mm.	200 mm.	100 mm.	50 mm.	25 mm.	10 mm.	Watts per cm. carried by nitrogen. 750 mm.	200 mm.	100 mm.	50 mm.	10 mm.	1 mm.
800	0.01	0.49	1.70	1.20	1.03	...	0.68	..	..	..	.	..	..	..
900	0.01	0.57	2.15	1.50	1.29	...	0.80	..	..	..	..	..	..	..
1000	0.02	0.65	2.60	1.80	1.52	...	0.95	..	..	..	..	..	..	..
1100	0.03	0.72	3.02	2.10	1.80	...	1.09	..	..	..	0.40	..	..	..
1200	0.05	0.80	3.50	2.46	2.05	...	1.25	..	..	..	0.48	..	..	..
1300	0.08	0.87	4.08	2.86	2.17	...	1.44	..	..	..	0.58	..	..	0.09
1400	0.11	0.95	4.72	3.33	2.70	...	1.65	..	..	..	0.67	..	0.30	0.10
1500	0.15	1.03	5.50	3.90	3.13	...	1.92	..	..	..	0.78	..	0.34	0.11
1600	0.21	1.11	6.32	4.45	3.64	...	2.20	..	..	..	0.90	..	0.38	0.12
1700	0.29	1.20	7.15	5.10	4.22	...	2.50	..	..	..	1.01	..	0.44	0.13
1800	0.38	1.29	8.04	5.75	4.88	...	2.92	..	..	..	1.12	..	0.50	0.13
1900	0.50	1.39	9.02	6.49	5.64	...	3.6	...	..	..	1.22	..	0.56	0.14
2000	0.65	1.49	10.17	7.38	6.63	...	4.4	2.6	1.65	1.46	1.34	1.00	0.60	0.14
2100	0.83	1.59	11.56	8.44	7.85	7.1	5.4	3.4	1.86	1.60	1.45	1.08	0.64	0.15
2200	1.06	1.69	13.2	9.74	9.42	9.1	6.9	4.6	2.06	1.76	1.58	1.16	0.68	0.15
2300	1.31	1.79	15.2	11.2	11.4	11.6	8.9	6.0	2.26	1.91	1.73	1.25	0.72	0.16
2400	1.60	1.89	17.5	13.4	14.3	14.9	11.4	8.0	2.46	2.06	1.87	1.34	0.75	0.16
2500	1.92	1.99	20.7	16.4	17.8	19.0	14.5	0.2	2.68	2.22	2.00	1.42	0.78	0.16
2600	2.33	2.09	24.2	19.9	21.5	23.6	18.5	13.4	2.90	2.36	2.14	1.51	0.81	0.17
2700	2.70	2.20	28.8	25.5	27.6	29.8	23.5	17.0	3.12	2.52	2.27	1.60	0.84	0.17
2800	3.30	2.30	34.8	32.5	35.3	38.0	29.7	22.3	3.34	2.68	2.43	1.69	0.89	0.17
2900	3.86	2.41	41.1	42.0	45.1	46.5	36.7	27.2	3.56	2.84	2.58	1.78	0.96	0.18
3000	4.46	2.52	49.2	54.0	56.7	57.1	45.1	33.4	3.84	3.00	2.72	1.87	1.01	0.18
3100	5.13	2.62	58.0	67.0	70.4	68.6	55.0	41.6	4.06	3.16	..	1.97	..	..
3200	5.98	2.72	70.0	84.0	88.2	84.0	65.0	49.8	4.30	3.32	..	2.06	..	..
3300	6.94	2.82	82.0	101.0	110.0	101.0	79.0	60.0	4.54	3.49	..	2.16	..	..
3400	8.08	2.93	94.0	115.0	132.0	118.0	...	..	4.76	3.66	..	2.26	..	..
3500	9.41	3.05	108.0	136.0	....	...	...	..	5.00	3.83	..	2.36	..	..

in the effects in the two gases. In nitrogen, the values decrease steadily as the pressure is reduced, and in hydrogen, at the lower temperatures, the same decrease is observed. But at higher temperatures, in hydrogen, the power consumption is considerably greater at lower pressures than at atmospheric pressure.

The conclusions drawn from these measurements will be considered later, together with the results obtained at still lower pressures.

Lower Pressures.—In these experiments, measurements of the power consumption were made at a series of temperatures, with pressures ranging from 0.01 mm. up to 13 mm. The measurements were made while the lamps containing the filaments were connected to a vacuum system consisting of two McLeod gages (one for lower and one for higher pressures) and a Gaede mercury pump. The lamps were first exhausted at 360° for an hour and a trap immersed in liquid air placed directly below the lamps condensed the moisture given off from the glass.

The candle power was measured during the experiments by a portable Weber photometer. The characteristics in vacuum at temperatures ranging from 1500 to 2500° K. were first determined and then a few centimeters (pressure) of pure hydrogen was admitted to the system and pumped out to a pressure of 13 mm. A series of measurements of current, voltage and candle power was again made. In this way, in the first experiment, the characteristics were measured at pressures of 13.1, 6.5, 2.5, 1.2, 0.53, 0.218, 0.102 and 0.045, 0.020 and 0.010 mm. and at 0.0001 mm. In a second experiment, measurements at a few pressures were made as a check on the preceding.

In the third experiment, made a few weeks later, a much more complete series of measurements was made, extending the range of observations from 1100° to 2900° K. Higher temperatures were avoided, in order not to cause any evaporation of the filament. The pressures employed in this set of tests were 4.4, 1.10, 0.207, 0.039, 0.015, and 0.00007 mm. At each pressure about 30 readings at different temperatures were taken.

The results of the third experiment were in excellent agreement with those of the first two. Since the former covered so much wider a range, only these results are given in this paper.

The tungsten wire used for these experiments was taken from the same spool as that used in the experiments at higher pressures.

The filament was mounted horizontally in a straight piece 9.85 cm. long. Because of the cooling effect of the leads, it was assumed that the effective length of the wire for calculation of the watts per centimeter was 9.4 cm. The bulb was a cylindrical bulb with rounded ends, about 10 cm. diameter and 18 cm. long, and the filament was supported in its axis.

TABLE II

			Heat carried by hydrogen watts per cm.				
Temp. ° K.	W_R.	R.	4.40 mm.	1.10 mm.	0.207 mm.	0.039 mm.	0.015 mm.
1100	0.022	0.60	0.26	0.09	0.020	0.004	0.002
1200	0.037	0.70	0.31	0.11	0.024	0.005	0.002
1300	0.060	0.80	0.36	0.13	0.030	0.006	0.002
1400	0.095	0.89	0.41	0.16	0.038	0.007	0.003
1500	0.138	0.98	0.47	0.19	0.050	0.009	0.004
1600	0.192	1.07	0.55	0.22	0.066	0.012	0.006
1700	0.268	1.15	0.65	0.28	0.088	0.019	0.008
1800	0.36	1.24	0.82	0.36	0.125	0.032	0.012
1900	0.48	1.33	1.09	0.52	0.21	0.06	0.019
2000	0.62	1.42	1.44	0.85	0.34	0.10	0.031
2100	0.78	1.52	2.06	1.27	0.53	0.16	0.055
2200	0.98	1.62	2.98	1.81	0.73	0.22	0.092
2300	1.23	1.72	4.37	2.62	0.99	0.29	0.120
2400	1.55	1.82	5.98	3.56	1.27	0.37	0.148
2500	1.82	1.92	8.21	4.85	1.58	0.42	0.178
2600	2.20	2.02	11.0	5.49	1.82	0.48	0.189
2700	2.67	2.12	..	6.23	1.96	0.50	0.191
2800	3.20	2.23	..	6.97	1.98	0.50	0.191
2900	3 80	2.34	..	7.61	1.99	0.50	0.191

The data obtained by these experiments are given in Table II. In the second and third columns are given the characteristics of the filament in good vacuum (0.00007 mm.). W_R is expressed in watts per centimeter, and R in ohms per centimeter. The figures in the other columns give the differences between the observed power consumption at different pressures and those in vacuum.

DISCUSSION OF EXPERIMENTAL RESULTS

The experimental data contained in Table I and II give, as a function of both temperature and pressure, the total heat carried by the surrounding hydrogen from a heated tungsten filament in this gas.

It has been shown in the previous papers that this energy carried by the gas can be resolved into two parts, W_C and W_D.

$$W = W_C + W_D \tag{1}$$

The temperature coefficient of W_C is given by

$$W_C = S(\varphi_2 - \varphi_1) \tag{2}$$

where

$$\varphi = \int_0^T k dT.$$

In the previous paper, S was calculated from results obtained with gases other than hydrogen. This method of calculation of S, although giving an approximation good enough for most purposes, may be open to criticism. In the present case, therefore, it has been thought better to determine S directly from the experimental results of Tables I and II.

The values of $\varphi_2 - \varphi_1$ were taken from the data given in the previous paper,[14] in which φ was calculated from the heat conductivity of hydrogen as determined by Eucken[15] and from the measurements of the viscosity of hydrogen by Fisher.[16]

By trial a value of S was found, which, when multiplied by $\varphi_2 - \varphi_1$, would give the best agreement with the values of W observed at temperatures so low that W_D was negligible. At higher temperatures, W_D was obtained by subtracting $S(\varphi_2 - \varphi_1)$ from W. The logarithum of W_D was plotted against 1/T from the data at rather low temperatures (1700–2500° K.). It is only in this range of temperatures that the calculated values of W_D are materially affected by errors in the value S. By trial a value of S was finally chosen which would give most nearly a straight line relation between log W_D and 1/T.

These values of S have been used to calculate W_D and the results are given in Table III.

The results in Table III were obtained from the data in Table I and II, merely by subtracting the product of S (given at the head of each column of Table III) by $\varphi_2 - \varphi_1$ (given in second column of Table III).

The data on the heat losses from tungsten wires in nitrogen given in Table I, was used in a similar way to calculate $W - W_C$ and the results are given in Table IV. The values of $\varphi_2 - \varphi_1$ in this table are calculated from the viscosity and heat conductivity of nitrogen.[17]

A comparison of Tables III and IV shows clearly the very great difference between hydrogen and nitrogen. With nitrogen the heat loss increases with the temperature very nearly proportionally to $\varphi_2 - \varphi_1$. The differences observed and tabulated are not greater than the possible experimental errors. In the case of hydrogen, up to temperatures of 1500–1700° K., the results are similar to those of nitrogen; that is, there is no evidence that the differences between W and W_C are anything more than experimental errors. But at very high temperatures W_D increases very rapidly, and becomes 50 or 100 times as large as the possible experimental error.

In the second part of this paper, these data will be used to calculate the

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[14] *Physic. Rev., l. c.*

[15] *Physik. Z., 12,* 1101 (1911).

[16] *Physic. Rev., 24,* 385 (1907).

[17] See *Physic. Rev., l. c.*

TABLE III

W_D FROM EXPERIMENTS WITH HYDROGEN

Temp. ° K.	$\varphi_2-\varphi_1$ watts per cm.	750 mm. S= 1.25.	200 mm. S= 0.88.	100 mm. S= 0.72.	50 mm. S= 0.56.	25 mm. S= 0.40.	10 mm. S= 0.21.	4.40 mm. S= 0.096.	1.10 mm. S= 0.040.	0.207 mm. S= 0.009.	0.039 mm. S= 0.002.	0.015 mm. S= 0.0008.
800	1.23	+0.10	+0.13	+0.10	...	+0.17	..	..	..	...	...	...
900	1.68	+0.05	+0.02	+0.07	...	+0.13	..	..	..	...	...	...
1000	2.05	+0.04	0.00	+0.04	...	+0.13	..	..	..	...	...	...
1100	2.50	—0.10	—0.10	—0.01	...	+0.09	..	+0.02	—0.01	—0.002	—0.001	0.000
1200	3.00	—0.25	—0.18	—0.12	...	+0.05	..	+0.02	—0.01	—0.003	—0.001	0.000
1300	3.45	—0.24	—0.18	—0.32	...	+0.06	..	+0.03	—0.01	—0.001	—0.001	+0.001
1400	3.95	—0.22	—0.15	—0.16	...	+0.07	..	+0.03	0.00	+0.002	—0.001	0.000
1500	4.50	—0.13	—0.06	—0.13	...	+0.12	..	+0.04	+0.01	+0.009	+0.000	0.000
1600	5.05	+0.01	0.00	—0.02	...	+0.17	..	+0.07	+0.02	+0.020	+0.002	+0.002
1700	5.65	+0.09	+0.13	+0.12	...	+0.24	..	+0.11	+0.05	+0.037	0.008	+0.003
1800	6.28	+0.19	+0.23	+0.33	...	+0.41	..	+0.22	0.11	0.068	0.019	+0.007
1900	6.93	+0.35	+0.39	0.61	...	0.8	..	0.43	0.24	0.15	0.05	0.013
2000	7.62	+0.64	+0.67	1.10	...	1.3	1.0	0.71	0.54	0.27	0.09	0.025
2100	8.34	1.15	1.10	1.8	2.4	2.1	1.7	1.26	0.94	0.45	0.14	0.048
2200	9.13	1.80	1.70	2.8	4.0	3.2	2.7	2.10	1.45	0.65	0.20	0.085
2300	9.90	2.8	2.5	4.2	6.1	4.9	3.9	3.42	2.22	0.90	0.27	0.112
2400	10.70	4.2	4.0	6.5	8.9	7.1	5.8	4.95	3.13	1.17	0.35	0.139
2500	11.53	6.3	6.3	9.4	12.5	9.9	7.8	7.10	4.19	1.48	0.40	0.169
2600	12.36	8.8	9.0	12.5	16.7	13.5	10.8	9.8	5.00	1.71	0.45	0.179
2700	13.28	12.2	13.8	18.0	22.4	18.2	14.2	..	5.7	1.84	0.47	0.180
2800	14.22	17.0	20.0	25.0	30.0	24.0	19.3	..	6.4	1.85	0.47	0.180
2900	15.22	22.0	29.0	34.0	38.0	30.0	24.0	..	7.0	1.85	0.47	0.180
3000	16.20	29.0	40.0	45.0	48.0	38.6	30.0	..	..	..	..	...
3100	17.13	37.0	52.0	58.0	59.0	48.1	38.0	..	..	..	.	...
3200	18.17	47.0	68.0	75.0	74.0	58.0	46.0	..	..	..	..	...
3300	19.21	58.0	84.0	96.0	90.0	71.0	56.0	..	..	..	..	...
3400	20.35	69.0	97.0	117.0	107.0	....	..	..	..	..	..	...
3500	21.50	81.0	117.0	....	...	....	..	..	..	..	..	...

TABLE IV

"W_D" FROM EXPERIMENTS WITH NITROGEN

T_1 °K.	$\varphi_2 - \varphi_1$ watts per cm.	750 mm. S= 1.41.	200 mm. S= 1.15.	100 mm. S= 1.06.	50 mm. S= 0.75	10 mm. S= 0.43.	1 mm. S= 0.10.
1100	0.43	....	....	−0.06	....	....	....
1200	0.49	....	....	−0.04	....	....	....
1300	0.56	....	....	−0.01	....	....	+0.03
1400	0.63	....	....	−0.04	....	+0.03	+0.04
1500	0.73	....	....	+0.01	....	+0.03	+0.04
1600	0.82	....	....	+0.03	....	+0.03	+0.04
1700	0.92	....	....	+0.03	....	+0.04	+0.04
1800	1.03	....	....	+0.03	....	+0.06	+0.03
1900	1.13	....	....	+0.02	....	+0.07	+0.03
2000	1.25	−0.11	+0.02	+0.01	+0.07	+0.06	+0.02
2100	1.36	−0.04	+0.04	+0.01	+0.06	+0.06	+0.01
2200	1.49	−0.01	+0.05	0.00	+0.04	+0.04	0.00
2300	1.61	−0.01	+0.06	+0.02	+0.05	+0.03	0.00
2400	1.74	+0.01	+0.06	+0.02	+0.04	+0.00	−0.01
2500	1.87	+0.04	+0.07	+0.02	+0.02	+0.02	−0.03
2600	2.02	+0.05	+0.04	−0.00	0.00	−0.06	−0.03
2700	2.16	+0.07	+0.04	−0.02	−0.02	−0.09	−0.05
2800	2.31	+0.08	+0.02	−0.03	−0.04	−0.10	−0.06
2900	2.47	+0.08	0.00	−0.04	−0.07	−0.10	−0.07
3000	2.63	+0.13	−0.02	−0.07	−0.10	−0.11	−0.08
3100	2.79	+0.12	−0.04	....	−0.12	....	....
3200	2.96	+0.13	−0.08	....	−0.16	....	....
3300	3.13	+0.13	−0.11	....	−0.29	....	....
3400	3.31	+0.09	−0.14	....	−0.22	....	....
3500	3.49	+0.08	−0.18	....	−0.26	....	....

degree of dissociation and the heat of formation of hydrogen molecules. The experiments at low pressures lead to a somewhat detailed knowledge of the mechanism of the reaction taking place in the surface of the wire.

THE DISSOCIATION OF HYDROGEN INTO ATOMS

PART TWO

CALCULATION OF THE DEGREE OF DISSOCIATION AND THE HEAT OF FORMATION

THE FIRST PART of this paper[1] dealt with experiments on the heat losses from fine tungsten wires in hydrogen at pressures ranging from 0.010 mm. up to atmospheric pressure. The results were given in a series of tables, and form the basis for the present calculation of the degree of dissociation and the heat of formation of molecular hydrogen.

[1] Langmuir and Mackay, *Jour. Amer. Chem. Soc.*, *36*, 1708 (1914).

The previous calculations of the dissociation of hydrogen [2] were based on the use of the equation

$$W_D = SDq_1c_1 \qquad (3)^3$$

as described in Part I. The equation itself rests on a firm foundation, but the assumptions previously made in applying it to experimental results are open to serious criticism.

In the first place, it was assumed that the diffusion coefficient D could be calculated with sufficient accuracy from some equations of the kinetic theory by the rather arbitrary choice of a value for the mean free path of hydrogen atoms through ordinary molecular hydrogen.

Secondly, it was assumed that the shape factor S in the above equation had the same value as that obtained from the data on the convection losses in hydrogen at temperatures below that at which dissociation occurred.

Thirdly, it was assumed that the hydrogen in the immediate vicinity of the tungsten wire was in chemical equilibrium at a temperature corresponding to that of the wire. In other words, c_1 was taken to be the equilibrium concentration at the temperature of the wire.

And finally, the value of q_1 was found by a method which itself involved any error occurring in D.

Each of the four factors in Equation 3 was therefore liable to error. This was realized and pointed out at the time the calculations were made, but there was then no reason to suspect that any of these sources of error was serious enough to greatly affect the results.

In the present paper we shall endeavor to avoid these arbitrary assumptions and, by a careful analysis of the mechanism of the phenomena occurring in and around the wire, we will attempt to estimate and eliminate the errors which would otherwise occur.

EFFECT OF CONVECTION CURRENTS

In the experiments with hydrogen at atmospheric pressure the effect of convection currents in heating the upper part of the bulb was very noticeable. But in the bulbs with 200 mm. pressure of hydrogen or less, the upper part of the bulb was not as strongly heated as the lower part. It is, in fact, well known that convection currents decrease rapidly in intensity as the pressure is lowered, also that in hydrogen they are very much less pronounced than in other gases. If one considers the cause of convection currents it is evident that the behavior of hydrogen is just what one should expect.

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[2] *Ibid., 34,* 860 (1912). This paper will hereafter be referred to as the "paper of 1912."

[3] For the derivation of this and some of the following equations, see Part I, or the "paper of 1912." The numbers of the equations are the same as those used in Part I.

The force producing convection currents is proportional to the difference in the densities of the ascending and descending currents of the gas. Since the density of a gas is equal to pM/RT it is readily seen that the force producing convection is thus proportional to

$$\frac{pM}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)=\frac{pM}{RT_1}\left(\frac{T_2-T_1}{T_2}\right).$$

This force is directly proportional to the density of the gas and to the fraction $(T_2-T_1)/T_2$. As T_2 becomes large this fraction approaches unity as a limit, so that, at very high temperatures, there is little tendency for convection to increase, and even this is largely counteracted by the increasing viscosity of the gas at high temperatures.

The experimental results themselves, however, furnish us with data by which we can estimate the effect of convection currents.

At temperatures below that at which perceptible dissociation of hydrogen occurs, we have seen that the heat losses from the filament are given fairly accurately by the equation (see Table III, Part I).

$$W_C = S(\varphi_2 - \varphi_1). \tag{2}$$

The shape factor S for concentric cylinders is equal to (*Phys. Rev.*, *34*, 407 (1912))

$$S = \frac{2\pi}{\ln b/d} \tag{7}$$

where b is the diameter of the film of gas around the wire through which conduction takes place and d is the diameter of the wire.

Let us now substitute the experimentally determined values of S from Table III in this equation, together with the known value of d (= 0.00706 cm.) and solve the equation for b. We thus find

p.	S.	b.
750 mm.	1.25	1.08 cm.
200	0.88	9.0
100	0.72	45.0
50	0.56	530.0

At atmospheric pressure the effective diameter of the film of conducting gas around the tungsten wire is about one centimeter, but at 200 mm. pressure the diameter is already 9 cm., which is larger than the diameter of the bulb (7 cm.). This means that the heat loss from the filament is actually less than if there were no convection currents and the ordinary laws of heat conduction could be applied. At lower pressures the heat loss becomes still less, although we know that the true heat conductivity of gases is independent of the pressure.

These considerations lead us to conclude that the effects of convection currents can be neglected even at pressures as high as 200 mm. We shall see that the decrease in the values of S at the lower pressures is due to a temperature discontinuity at the surface of the wire.

THE TEMPERATURE-DROP AT THE SURFACE OF THE WIRE

Kundt and Warburg,[4] in a study of the viscosity of gases at low pressures, showed, both experimentally and theoretically, that there is a certain apparent slipping of the gas along the surface. In gases at atmospheric pressure this effect is very small, but it varies inversely proportional to the pressure and thus becomes very important at low pressures. The thickness of the layer in which this slipping occurs is approximately equal to the mean free path of the gas molecules. Kundt and Warburg predicted, from the analogy between viscosity and heat conduction, that a corresponding discontinuity in temperature at the surface of a solid body would be observed in the case of heat conduction through gases at low pressure.

Over twenty years later Smoluchowski [5] actually observed and studied this temperature drop and developed the theory of it. The temperature drop occurred within a layer about equal in thickness to the free path of the molecules. Smoluchowski found that in some gases, particularly hydrogen, the amount of heat given up to the gas by a solid body was only a fraction of that which should be delivered if each molecule striking the surface reached thermal equilibrium with the solid before leaving it.

Smoluchowski developed the theory of this effect along the lines of two alternative hypotheses, which he denotes by A and B.

Hypothesis A is equivalent to that made more recently by Knudsen.[6] It assumes, when molecules of a temperature T_1 strike a surface at a higher temperature T_2, that the molecules leaving the surface have a temperature T which is intermediate between T_2 and T_1 and that the relation holds

$$T - T_1 = \alpha(T_2 - T_1) \tag{8}$$

where α is a number less than unity and is called by Knudsen the "accommodation coefficient."

Hypothesis B is similar to that originally used by Maxwell [7] in dealing with the slip of gases. It assumes that, of all the molecules striking the surface, a fraction, f, reaches thermal equilibrium with it, while the fraction $1 - f$ is reflected without change of temperature (or rather velocity).

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[4] *Pogg. Ann.*, *156*, 177 (1875).

[5] *Wied. Ann.*, *64*, 101 (1898); *Wien. Sitzungsber.*, *108*, 5 (1899); *Phil. Mag.*, *46*, 192 (1898).

[6] *Ann. Phys.*, *34*, 593 (1911).

[7] *Phil Trans*, *170*, 231 (1879)

The two methods give analogous, but quantitatively slightly different results. Smoluchowski [8] considers that the accuracy of experimental results has not yet been sufficient to distinguish between them, notwithstanding Knudsen's opinion to the contrary, and that in all probability the truth is intermediate between the two.

The formulas developed by Smoluchowski are only adapted to be applied to small differences of temperature and to heat conduction between surfaces whose radius of curvature is large compared to the mean free path of the molecules. In the present experiments, however, we are dealing with very small wires and with temperature drops of sometimes a thousand degrees or more, and we shall therefore need to derive the equations independently. We shall choose a simpler, although less rigorous method, based upon the same principles as those used by Smoluchowski. In this way we shall gain a clearer insight into the phenomena occurring around the wire and will be in a better position to apply simliar principles to the problem of calculating the degree of dissociation of the gas.

Theory of Heat Conduction from Small Wires.—Let us consider a small heated wire A (Fig. 1) placed in the axis of a large cylindrical bulb B of diameter *b*, containing gas at such low pressure that the effects of convection can be neglected. Let T_2 be the temperature of the wire and T_1 that of the bulb. If λ represents the length of the mean free path, then the distance which a molecule leaving the wire travels before colliding with other molecules is approximately λ.[9] On the other hand, the molecules striking the wire come from an average distance λ. Let us draw a circle, C (in Fig. 1), of diameter $d + 2\lambda$, around the wire, whose diameter is d and a similar circle D of diameter $b - 2\lambda$.

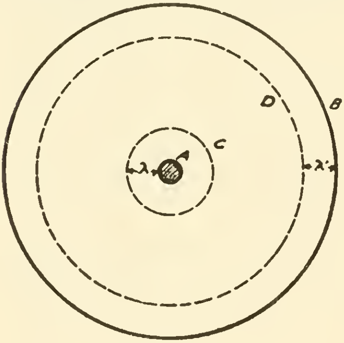

Fig. 1.

We may now look upon the heat conduction from the wire A to the cylinder B as taking place in the following steps:

1. Molecules of gas leave the wire and travel to C, where they are

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[8] *Ann. Phys., 35,* 983 (1911).

[9] Knudsen, *Ann. Phys., 34,* 654 (1911), shows that the temperature of the molecules striking a plane surface corresponds to the temperature of the gas at a distance equal to 0.95 times the mean free path of the molecules. Using more recent data than that available to Knudsen, I calculate from his formulas that this coefficient should be about 1.2. Undoubtedly the coefficient would be somewhat different for very small wires from what it is for plane surfaces, but in any case its order of magnitude is close to unity. Fairly large errors in the value of this coefficient make only very slight differences in the results that are to be obtained by its aid.

absorbed, and some molecules from C travel to the wire, a certain fraction of these absorbing heat from the wire.

2. From C to D the heat is carried according to the ordinary laws of heat conduction.

3. From D to B the energy is transferred by a simple interchange of molecules in a similar way to the transfer from A to C.

Thus we consider a temperature discontinuity from A to C and from D to B, but a continuous variation of temperature from C to D.

Since we are dealing with small wires in relatively large cylinders, we can readily see that the temperature drop from D to B will always be negligible compared to that from A to D. We shall therefore leave it out of consideration.

Let us represent by T_a the temperature of the gas at C. We can now calculate the temperature drop $T_2 - T_a$.[10]

If we let m be the rate at which the gas comes into contact with the wire (in grams per sq. cm. per second), then the heat carried from the wire per second will be (per cm. of length)[11]

$$W_C = 4.19\, \pi\, d\, (C_v/M)\, \alpha\, (T_2 - T_a) m. \tag{9}$$

Here C_v is the molecular heat at constant volume and the coefficient 4.19 converts calories to watt-seconds. The fraction α is the accommodation coefficient, and d is the diameter of the wire.

In order to calculate $T_2 - T_a$ from Equation 9 we must now substitute in it the value of m as given by Equation 5 of Part I, namely,

$$m = \sqrt{\frac{M}{2\pi R T_a}}\, p. \tag{5}$$

Here M is the molecular weight of the gas, T_a is the temperature of the gas at a distance λ from the wire (at C in Fig. 1).

In the derivation of this formula Maxwell's distribution law was assumed to hold. Where the temperature discontinuity at the surface is as large as in the present experiments the distribution of velocities among the molecules is undoubtedly very complex. The error involved in using this equation must, however, be relatively small.[12]

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[10] This is somewhat greater than the temperature drop defined by Smoluchowski, for it includes the *normal* temperature difference between A and C.

[11] Knudsen shows that this should be multiplied by 4/3, since the average velocity of all the molecules striking any surface is greater than the average velocity of the molecules in the body of the gas. This is due to the fact that the molecules of high velocity have a much greater chance of striking a surface than those of low velocity. On the other hand, for polyatomic gases the exchange of rotational energy is not complete and, therefore, a quantity less than should be substituted in the above equation. According to Smoluchowski, the combined effect of these two corrections would lead to a coefficient of 16/15 in place of the 4/3 mentioned above. For the present purpose this small correction may be neglected.

Before substituting (5) in (9) let us insert the numerical values of the constants. In (5) we place $M = 2$, $R = 8.32 \times 10^7$ ergs/° C. and express p in mm. of mercury and m in grams per sq. cm. per second. We thus obtain

$$m = \frac{0.0825\, p}{\sqrt{T_a}}. \tag{10}$$

In (9) we place $C_v = 5.26$ g. cals. per degree (from 300° to 1500° K.)[13] and $d = 0.00706$ cm. This gives, when we combine with (10)

$$T_2 - T_a = 49.6\, \frac{W_C \sqrt{T_a}}{\alpha p}. \tag{11}$$

This equation enables us to estimate the difference between the temperature of the wire and that of the gas molecules which strike its surface.

We may also calculate the temperature of the gas molecules striking the wire in another way. Between the surface C (Fig. 1) and the bulb, the ordinary laws of heat conduction must apply at pressures below that at which convection occurs. Thus we may place, according to (2) and (7)

$$W_C = \frac{2\pi}{\ln b/(d + 2\lambda)} (\varphi_a - \varphi_1). \tag{12}$$

If we know the effective diameter of the bulb and the mean free path of the gas molecules, we can calculate from this equation the value of $(\varphi_a - \varphi_1)$, and since φ is a known function of the temperature, this in turn will enable us to determine T_a.

Let us now calculate T_a from our experiments with hydrogen by means of Equations 11 and 12. For this purpose we will choose the data obtained at 1500° K., for at this temperature there is no appreciable dissociation and the temperature measurements are more accurate than at lower temperatures. These data, as taken from Table I and II of Part I, are given below in Table V in the second column. The figures represent the watts per centimeter carried by the hydrogen from a wire at 1500° K.

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[12] With large differences of temperature over distances comparable with the free path, another effect, which we may call the radiometer effect, enters to render Equation 5 inaccurate. The rapidly moving molecules leaving the wire tend to drive back the slower incoming molecules and thus to decrease the rate at which the molecules strike the wire. Although this effect would be very important if we were dealing with large flat surfaces, calculation shows that in our present experiments, where only fine wires are employed, this error is always less than 5% and usually much less than this. It has, therefore, been neglected.

[13] The letter K is used to denote temperatures on the absolute scale (Kelvin).

The first column gives the pressure of hydrogen in mm. of mercury. In the third column are the values of T_a calculated by Equation 11.

TABLE V

WIRE IN HYDROGEN

$T_2 = 1500.$ $\alpha = 0.19.$

1. p.	2. W_C.	3. T_a by (11).	4. λ cm.	5. $\varphi_a - \varphi_1$.	6. b.	7. T_a by (12).
750	5.50	1428	0.0001	[4.10]	0.78	(1428)
200	3.90	1316	0.0003	[3.53]	1.87	(1316)
100	3.13	1216	0.0006	[3.03]	3.7	(1216)
50	(2.52)	1071	0.0011	2.39	[3.7]	1070
25	1.92	900	0.0020	1.78	[3.7]	920
10	(0.94)	806	0.0037	0.83	[3.7]	660
4.4	0.47	742	0.0063	0.46	[9.0]	520
1.1	0.19	495	0.020	0.16	[9.0]	390
0.207	0.050	341	0.094	0.03	[9.0]	317
0.039	0.009	360	0.5	0.003	[9.0]	302
0.015	0.004	[300]	1.3	0.001	[9.0]	300

The accommodation coefficient α was calculated from the data at the lowest pressure (0.015 mm.) by substituting $T_a = 300$;[14] $T_2 = 1500$; $W_C = 0.004$; and $p = 0.015$ in Equation 11. This gave $\alpha = 0.19$, which, when substituted in (11) gave

$$T_2 - T_a = 260\,(W_C/p)\,\sqrt{T_a}. \tag{13}$$

The values of T_a given in the third column of Table V were obtained by solving these quadratic equations.

The free path of hydrogen molecules at 0° C. and 1 mm. pressure is 0.0135 cm., according to O. E. Meyer. The free path varies with the temperature according to Sutherland's formula, but for the present purpose it is accurate enough to assume that it is inversely proportional to the density. The fact that at low pressures the molecules leaving the filament travel through groups of molecules having a much lower temperature, introduces the necessity for a rather special calculation of the free path leading to the formula[15]

$$\lambda = \frac{49.5 \times 10^{-6}}{p}\,T_a \sqrt{\frac{2T_2}{T_2 + T_a}}. \tag{14}$$

This equation was used to calculate the free paths given in Col. 4 of Table V.

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[14] That it is justifiable to place $T_a = 300$ at these lowest pressures is shown by the results obtained below and given in the seventh column.

[15] Derived from the equations given on page 260 of Meyer's "Kinetische Theorie der Gase," German edition of 1899.

At the higher pressures the effects of convection currents cannot be neglected, so that Equation 12 would not be expected to hold accurately under these conditions. However, even in the case of convection from small wires in the open air we may profitably look upon the phenomena as consisting essentially in conduction through a film of stationary gas of a certain thickness. If we adopt this view-point, Equation 12 applies even at the higher pressures, but b then no longer represents the diameter of the bulb, but becomes the effective diameter of the film of gas through which conduction occurs. To determine the value of b we need only substitute the values of W_C, d, λ and $\varphi_a - \varphi_1$ in Equation 12 and solve for b. For this purpose the values of $\varphi_a - \varphi_1$ were calculated from T_a, for the pressures of 760 to 100 mm., and are given in Table V (Col. 5) in brackets. These then served to calculate b from (12). At the lower pressures (50–10 mm.) it was then assumed that convection currents were absent and that b was therefore independent of the pressure and equal to the value 3.7 cm., as found at 100 mm. Below 10 mm. b was placed equal to the diameter of the bulb, for in these experiments a straight wire in a cylindrical bulb was used.

The values of $\varphi_a - \varphi_1$ at the lower pressures were obtained from (12) by substituting in it W_C, b, d and λ as given in the table. The results are given in Col. 5 (without brackets) and were used to calculate the corresponding values of T_a given in the seventh column.

By comparison of Cols. 3 and 7, it is seen that there is reasonably good agreement between the values of T_a calculated by these entirely independent methods. The fact that the temperature drop at the surface of the wire ($T_2 - T_a$) is so large, even at the higher pressures, is the reason for the variation of the shape factor (given in Table III at the heads of the columns).

The accommodation coefficient α is found above to be equal to 0.19. This is considerably lower than the value 0.36 found by Knudsen for hydrogen in contact with polished platinum at approximately room temperature.

The results given in Col. 6 of Table V show that the effective thickness of the layer of "stationary" gas around the wire increases as the pressure decreases from 750 to 100 mm., owing to convection currents. At lower pressures, however, the results indicate that there is no further change in b. If the lamps used in these experiments had contained a long, straight filament in the axis of a cylindrical bulb, then b should be equal to the diameter of the bulb. Actually, however, the filament was a short loop only about 3 cm. long. The resulting divergence of the lines of heat flow would tend to increase the shape factor, which would be equivalent to a decrease in diameter of a cylindrical bulb. Hence the value of 3.7 cm. found above for b is in as close agreement with the actual bulb diameter (7 cm.) as the experimental conditions would seem to warrant.

Nitrogen.—Similar calculations from the data given in Table I, for a filament at a temperature of 2400° in nitrogen yield the results shown in Table VI. The values of T_a in Col. 3 were obtained from a formula similar to (11) in which, however, the coefficient 49.6 was replaced by 166, corresponding to the different molecular weight and specific heat of nitrogen. The columns of Table VI correspond exactly to those of Table V.

It is seen by the variation of b that the effect of convection is much more marked than with hydrogen and persists at pressures even as low as 50 mm.

TABLE VI

Wire in Nitrogen

$T_2 = 2400.$ $\alpha = 0.60.$

1. p.	2. W_C.	3. T_a.	4. λ cm.	5. $\varphi_a - \varphi_1$.	6. b.	7. T_a by (12).
750	2.46	2356	0.0001	[1.68]	0.54	(2356)
200	2.06	2264	0.0003	[1.56]	0.89	(2264)
100	1.87	2160	0.0006	[1.44]	1.01	(2160)
50	1.34	2064	0.0011	[1.32]	4.4	(2064)
10	0.75	1580	0.0046	0.74	[8]	1530
1	0.16	1000	0.031	0.12	[8]	650

The accommodation coefficient is much larger than that of hydrogen, but is again less than that given by Knudsen (for air) at room temperature.

The agreement between the values of T_a calculated by the two independent methods, in both Tables V and VI, is sufficiently good to show that the general theory of heat conduction and convection used in making the calculations can safely be applied to the case of fine tungsten wires in hydrogen and nitrogen at all pressures. Evidently the heat conductivities of these gases, within the ranges of temperature considered above, vary with the temperature in the way that is to be expected from their behavior at ordinary temperatures.

CONCENTRATION DROP AT THE SURFACE OF THE WIRE

We have seen that the temperature of the layer of gas next to the wire may be very much lower than that of the wire itself. To assume that these two temperatures are equal, which amounts to assuming temperature equilibrium at the surface of the wire, would lead to entirely erroneous results.

The diffusion of one gas through another is a phenomenon closely related to heat conduction. In the case of the evaporation of a solid surrounded by a gas, where the vapor must diffuse outward through the gas, the partial pressure of the vapor at the surface of the solid will be less than that of the saturated vapor. In other words, there will be a "concentration-drop" at the surface, just as there is a "temperature drop" in the analogous case of heat conduction, and a "slip" in gases where viscosity effects are involved. Analogy suggests that this concentration drop will be inversely proportional to the pressure.

In the previous calculations of the dissociation of hydrogen it was assumed that the concentration of the hydrogen atoms close to the wire, was that corresponding to equilibrium at the temperature of the wire. As the experiments underlying these calculations were made at atmospheric pressure, this assumption involved no serious error, but at the low pressures which we are now to consider, such an assumption would render the results worthless.

In analyzing the effect of the surface concentration drop in our present experiments, we may follow methods entirely analogous to those which we adopted in estimating the temperature drop.

Let us consider the mechanism of the phenomena occurring on and around a tungsten wire surrounded by hydrogen, and heated to such a high temperature that the hydrogen is partly dissociated. The hydrogen molecules striking the surface come from an average distance of approximately λ (the mean free path). A certain proportion of these molecules leave the surface without change (reflected) and another portion is absorbed by the wire and may thus be dissociated. Similarly, hydrogen atoms striking the filament may be absorbed or reflected. The hydrogen which is absorbed probably reaches chemical equilibrium within the wire and the atoms and molecules in certain proportions diffuse out and away from the wire. We assume that the hydrogen not absorbed undergoes no chemical change.

Let m_2 represent the rate at which hydrogen molecules strike the surface of the filament (in grams per sq. cm. per second) and m_1 be the corresponding rate for the hydrogen atoms. Let $\alpha_1 m_1$ be the rate at which the hydrogen atoms are absorbed by the wire and $\alpha_2 m_2$ be the rate at which the molecules are absorbed. Now in a stationary condition the total amount of hydrogen escaping from within the wire must be equal to the rate at which it is absorbed. We may look upon the surface of the wire as the boundary of a space containing hydrogen in equilibrium. The rate at which the hydrogen atoms in the metal reach the surface (from within) we shall call n_1, and the corresponding rate for the molecules n_2. Similarly, we shall let $\beta_1 n_1$ be the rate at which atoms escape from the metal and $\beta_2 n_2$ the rate at which molecules escape. Then in a stationary state we have

$$\beta_1 n_1 + \beta_2 n_2 = \alpha_1 m_1 + \alpha_2 m_2. \tag{15}$$

We assume that the coefficients α and β are constant; that is, that they are independent of m and n, although they may vary with the temperature.

The energy (watts) carried away from the wire (per cm.) because of the dissociation, we have called W_D. If q_1 be the heat (calories) necessary to dissociate 1 g. of hydrogen, then we have

$$W_D = 4.19\,\pi\,d\,q_1\,(\alpha_2 m_2 - \beta_2 n_2). \tag{16}$$

Here d is the diameter of the wire. The quantity in parenthesis is the difference between the rates at which hydrogen molecules are absorbed and are given up by the wire and therefore is equal to the rate at which hydrogen is dissociated.

If we place

$$\omega = W\,/(4.19\,\pi\,d\,q_1) \tag{17}$$

then (16) becomes

$$\omega = \alpha_2 m_2 - \beta_2 n_2 \tag{18}$$

Combining this with (15), we obtain

$$\omega = \beta_1 n_1 - \alpha_1 m_1 \tag{19}$$

whence

$$\begin{cases} \beta_1 n_1 = \alpha_1 m_1 + \omega \\ \beta_2 n_2 = \alpha_2 m_2 - \omega \end{cases} \tag{20}$$

Now we have assumed that equilibrium exists between the hydrogen atoms and molecules absorbed by the wire. According to the law of mass action, the concentration of the hydrogen molecules in the metal is proportional to the square of the concentration of the atoms. But n_2 and n_1 must be proportional to these concentrations. From Equation 20 we thus obtain

$$(\alpha_1 m_1 + \omega)^2 = A(\alpha_2 m_2 - \omega). \tag{21}$$

Here A is a constant which is proportional to the dissociation constant of hydrogen dissolved in the metal. We may now obtain a relation between this quantity A and the true dissociation constant K of gaseous hydrogen (outside the wire).

We have

$$K = (p'_1)^2/p'_2 \tag{22}$$

where p'_1 and p'_2 are, respectively, the partial pressures of hydrogen atoms and molecules corresponding to equilibrium in the gaseous phase.

By Equation 5 (Part I) we have from (22) by placing $M_1 = 1$ and $M_2 = 2$

$$K = \sqrt{4\pi R T_2}\,(m'_1)^2/m'_2 \tag{23}$$

where T_2 is the temperature of the filament.

On the other hand, if we place $\omega = 0$ in (21), we obtain the condition for equilibrium. In this case (21) becomes

$$A = (\alpha_1^2/\alpha_2) \cdot (m_1')^2/m_2' \tag{24}$$

and by combining this with (23) we find the desired relation between A and K

$$K = \sqrt{4\pi RT_2}\,(\alpha_2/\alpha_1^2)\,A. \tag{25}$$

If we now substitute in (21) the values of m_1 and m_2 from Equation 5 and then combine with (25), we obtain

$$K = \sqrt{T_2/T_a}\,\frac{(p_1 + \omega\sqrt{2\pi RT_a}/\alpha_1)^2}{p_2 - \omega\sqrt{2\pi RT_a}/\alpha_2\sqrt{2}}. \tag{26}$$

Here T_a is the temperature of the gas around the wire at a distance λ from it (corresponding to circle C of Fig. 1). When $\omega = 0$ and $T_a = T_2$ this equation reduces to the ordinary form of the law of mass action. The "drop in concentration" corresponding to the drop in temperature previously considered is equivalent to $\omega\sqrt{2\pi RT_a}/\alpha_1$.[16]

In the above equation p_1 and p_2 are the partial pressures of hydrogen atoms and molecules at a distance λ from the wire.

Let us substitute the numerical values of the constants involved in (26). If we express p in mm. of mercury, then the factor $\sqrt{2\pi R}$ is 17.15. If we place $d = 0.00706$ cm. (the diameter of the wire) in (17) we find $\omega = 10.8\ W_D/q_1$. Substituting these in (26), we obtain

$$K = \sqrt{T_2/T_a}\;\frac{(p_1 + 185.W_D\sqrt{T_a/\alpha_1 q_1})^2}{p_2 - 131\ W_D\sqrt{T_a/\alpha_2 q_1}}. \tag{27}$$

Here p is expressed in mm., W_D in watts per cm., and q_1 in calories per gram.

DIFFUSION OF ATOMIC HYDROGEN AWAY FROM THE WIRE

In the calculation of the temperature drop around a wire in hydrogen, we used two methods which led to Equations 11 and 12, respectively. Similarly, in the calculation of the concentration drop, two methods may be used. The method adopted above in obtaining Equation 27 is analogous to that used in deriving (11), whereas the following method corresponds to that employed in obtaining (12).

In the "paper of 1912" it was shown that

$$W_D = SDq_1c_1 \tag{3}$$

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[16] Expressed as partial pressure instead of concentration.

Here c_1 is to be expressed in mols per cc., and is equal to

$$c_1 = p_1/RT. \tag{28}$$

The diffusion coefficient varies with the temperature according to Sutherland's formula, but at the high temperatures we are dealing with, this becomes equivalent to stating that the diffusion coefficient varies with the 3/2 power of the temperature. We will assume that the diffusion coefficient of hydrogen atoms through molecular hydrogen varies in this way with the temperature, although we shall avoid assumptions as to its actual magnitude. Since the diffusion coefficient is inversely proportional to the pressure, we may thus place:

$$D = D_0(T_a/273)^{3/2}.(760/P) \tag{29}$$

where D_0 is the diffusion coefficient at 0° and 760 mm. pressure, and T_a is the temperature of the gas around the wire (*i.e.*, at the distance λ from it).

Combining (29), (28), and (3) we obtain, after substituting the numerical value for R

$$W_D = 11.3 \times 10^{-6}\ Sq_1D_0\sqrt{T_a}\ p_1/P. \tag{30}$$

This equation gives us the desired relation between p_1, the partial pressure of hydrogen atoms around the wire, and W_D. It enables us to calculate the degree of dissociation if we know S, q_1 and D_0.

EQUATIONS INVOLVED IN CALCULATING THE DISSOCIATION CONSTANT, ETC.

Equation 27 has given us a means of calculating the dissociation constant from the partial pressures of hydrogen atoms and molecules around the wire. These partial pressures may be expressed in terms of the diffusion constant by means of Equation 30. By combining these two equations it is possible to obtain a general solution of the problem in the following form:

$$K = \sqrt{T_2/T_a}\ \frac{W^2_D(BP + E)^2}{P - W_D(BP + C)} \tag{31}$$

where

$$B = 88500/(SD_0q_1\sqrt{T_a}) \text{ cm. per watt} \tag{32}$$

$$C = 131\sqrt{T_a}/(\alpha_2q_1) \text{ mm. of Hg per watt/cm.} \tag{33}$$

$$E = 185\sqrt{T_a}/(\alpha_1q_1) \text{ mm. of Hg per watt/cm.} \tag{34}$$

The dissociation constant K increases rapidly with the temperature, while B, C and E depend only to a small degree on the temperature, and therefore we see by (31) that at low temperatures W_D will increase approximately proportional to $\sqrt{K}$. At high temperatures, however, the two terms in the denominator must tend to become equal, so that W_D would approach a limiting value. From Equation 31 we can readily derive simple equations for these limiting cases.

At low temperatures the second term of the denominator is negligible, so that

$$K = \sqrt{T_2/T_a}\,W_D^2(BP + E)^2/P. \qquad (35)$$

At low pressures this gives:

$$W_D = \sqrt[4]{\frac{T_a}{T_2}}\sqrt{\frac{PK}{E}}. \qquad (36)$$

At high pressures (here $T_a = T_2$).

$$W_D = \sqrt{K/P}/B. \qquad (37)$$

At intermediate pressures W_D increases to a maximum. Differentiating (35) with respect to P and placing $dW_D/dP = 0$ leads to following maximum value of W_D (here $T_a = T_2$):

$$W_{\text{max.}} = \sqrt{K/4BE}. \qquad (38)$$

The pressure at which this maximum occurs is

$$P' = E/B. \qquad (39)$$

At high temperatures W_D increases so that ultimately $W_D(BP + C)$ becomes nearly equal to P. Beyond this value it cannot go. Therefore, at high temperatures W_D must gradually approach a limiting value. This limit is

at low pressures

$$W_D = P/C \qquad (40)$$

at high pressures

$$W_D = 1/B. \qquad (41)$$

The higher the pressure the higher is the temperature at which W_D approaches its limiting value.

We shall see that the case where $C = E$ is of special importance. If we make this substitution in (31) and place

$$F = BP + E \qquad (42)$$

we obtain the very simple equation

$$K = \sqrt{T_2/T_a}\,\frac{F^2W^2_D}{P - FW_D}. \qquad (43)$$

At higher pressures T_a becomes practically equal to T_2, so the equation is still further simplified.

$$K = F^2W^2_D/(P - FW_D). \qquad (43a)$$

Comparing this with (22), we see that FW_D is equal to the partial pressure of hydrogen atoms corresponding to equilibrium at the temperature of the filament. The degree of dissociation of the hydrogen in equilibrium is therefore FW_D/P.

At low temperatures we have already found expressions for the maximum value of W_D and the pressure at which this occurs. On the assumption that $C = E$ we may now find more general expressions applicable even at high temperatures. Differentiating (42) and (43a) with respect to P, placing $dW_D/dP = 0$ and solving the resulting equation together with (31), we obtain

$$W_{\text{max.}} = 1/(B + \sqrt{4BE/K}). \qquad (44)$$

$$P' = (E/B) + \sqrt{EK/B}. \qquad (45)$$

CALCULATION OF RESULTS FROM EXPERIMENTAL DATA

The equations that have been derived in the preceding section give us means of calculating the coefficients B, C and E, and in this way of determining the dissociation constant K. Thus from the experiments at low pressures and at low temperatures it should be possible by (36) to find the ratio $\sqrt{K}:E$. Experiments at high pressures give by (37) $\sqrt{K}:B$, while those at high temperatures and low pressures give C according to (40). At high pressures and high temperatures we should then obtain B by (41). By combining these results it would thus be possible to find the actual values of B, C, E and K, separately. In practice, however, this method gives difficulty, because the experiments do not cover a sufficiently wide range of pressures or temperatures to allow these limiting equations to hold accurately. Furthermore, the values of W_D obtained under the extremes of temperature or pressure are often subject to unusually large experimental error, and it is unwise to use such data exclusively for the determination of the coefficients. A third difficulty is that Equations 36, 37, 40, and 41 all involve to some extent T_a, the temperature of the gas around the wire, which is not accurately known.

The method finally adopted to determine the coefficients B, C and F has been chosen because of its relative freedom from these difficulties.

1. *The Value of C.*—According to our theory, at very low pressures, W_D does not increase indefinitely with rising temperature, but approaches a limiting value equal to P/C (Equation 40). If we examine the experimental data of Table III we see, in fact, that W_D at the three lower pressures, 0.015, 0.039 and 0.207 mm., becomes constant at temperatures over 2700°. This is also readily seen from Fig. 2, in which log W_D has been plotted against 1/T. The limiting value of W_D at high temperatures for

each of these pressures is given in the following table, along with the ratio P/W_D, which, according to (40), is equal to C:

TABLE VII

P.	W_D.	$C = P/W_D$.	T_a.
0.015	0.18	0.0835	300
0.039	0.47	0.083	300
0.207	1.85	0.112	545

The constancy of C at the lower pressures and its increase at the higher pressure, is in full accord with Equation 33, which states that C is proportional to $\sqrt{T_a}$. At very low pressures T_a must be equal to the temperature of the bulb (300° K.), just as it was at lower filament temperatures (see Table V). At higher pressures, however, where the hydrogen atoms recombine long before reaching the surface of the bulb, the heat evolved raises the temperature of the gas considerably. At the lower pressures, however, we may safely place $T_a = 300$, and we then find, by comparing Table VII with Equation 33:

$$C = 0.0048\sqrt{T_a} \tag{46}$$

$$\alpha_2 q_1 = 27300 \tag{47}$$

This indicates, since by definition α_2 cannot exceed unity, that q_1 must be greater than 27300, or the heat of formation of 2 g. of hydrogen molecules, must be greater than 54600 calories.

If we compare (46) with the value $C = 0.112$ obtained for $P = 0.207$, we find $T_a = 545$. This is, as we shall see later, an entirely reasonable value.

2. *Calculation of an Approximate Value of* q_1.—If we can determine q_1 then by (47) we can calculate α_2. This will, in a certain measure, give us a check on our theory, for we know that α_2 cannot exceed unity.

To calculate q_1 we may make use of van't Hoff's equation

$$d \ln K/dT = q/RT^2. \tag{48}$$

Here q is the heat of reaction at constant pressure since K is expressed in terms of partial pressures. The relation between q and q_1 is

$$q = 2q_1 + RT. \tag{49}$$

If we use ordinary logarithms in place of naperian and substitute $R = 1.98$ calories, we may write Equation 48 as follows:

$$d \log K/d(1/T) = -q/4.57 \tag{50}$$

Since q varies so little with the temperature, we should, according to (50), obtain practically a straight line if we plot log K against $1/T$. The slope of the line would then be $q/4.57$, from which, by (49), we could calculate q_1. The slope of this line, however, would be the same if we plot the logarithm of any quantity proportional to K, instead of the logarithm of K itself. If we could assume that $T_a = T_2$ and that B and E were independent of the temperature, then we see from (35) that W^2_D should be proportional to K. The values of q_1 that we might thus obtain by plotting log W^2_D would not be very accurate, because the above assumptions are not strictly correct. However, by using Equation 38, which gives us a relation between K and $W_{max.}$ we avoid these difficulties. By (32) and (34) we see that the factor BE is independent of T_a and T_2, so that K is strictly proportional to $W_{max.}$. Another important advantage in using this equation in determining q is that it does not involve a knowledge of the pressure within the bulb. It should be remembered that in the experiments at pressures of 10 mm., and above, the pressures of the hydrogen as given in Table III were not measured while the filaments were heated, but were the pressures at which the bulbs were sealed at room temperature. The actual pressures in the bulbs during the experiment must have been considerably higher.[17]

It is clear, however, that this uncertainty in the pressure does not affect $W_{max.}$ nor the accuracy of K calculated from it by (38).

By examining Table III we see, as the pressure increases, that W_D increases to a maximum and then decreases. In the following table are the maximum values of W_D corresponding to various temperatures as given in Table III:

TABLE VIII

T.	$W_{max.} = \sqrt{K/4BE}$.	T.	$W_{max.} = \sqrt{K/4BE}$.
2000	1.3	2500	12.5
2100	2.4	2600	16.7
2200	4.0	2700	22.7
2300	6.1	2800	30.0
2400	8.9		

By plotting 2 log $W_{max.}$ against $1/T$ we obtain in fact an almost perfectly straight line. From the slope of this line we calculate by (50) that $q = 85500$ calories. If we take $T_2 = 2400$ (the center of the range of temperatures in the experiments), we then find by (49)

$$q_1 = 40300 \text{ calories.} \tag{51}$$

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[17] In some of the experiments at a pressure of 100 mm. of hydrogen, the bulbs became so hot at the higher filament temperatures that the glass softened and sucked in slightly. In another experiment the bulb was immersed in water to keep it cool. This cooling did not have any perceptible effect on the value of W_D.

3. *Calculation of* α_2 *and Lower Limit for E.*—Substituting (51) in (47), we obtain

$$\alpha_2 = 0.68. \tag{52}$$

This means that 68% of all the hydrogen molecules which strike the filament at high temperatures are absorbed by the filament.

If we substitute (51) in (34), we obtain

$$E = 0.0046\sqrt{T_a}/\alpha_1. \tag{53}$$

Since α_1 cannot exceed unity, E must be greater than $0.0046\sqrt{T_a}$.

The coefficient α_1 gives the fraction of the hydrogen atoms striking the filament which dissolve in it or are absorbed by it. There is a strong probability that this fraction should be very close to unity, for there is every reason to think that hydrogen atoms would be absorbed by a metal surface much more readily than the molecules, and we have just seen that 68% of the latter are absorbed. We shall see, however, that there is another way of estimating the value of α_1.

4. *Upper Limit for B.*—According to (41), the limit which W_D approaches at high temperatures does not increase indefinitely with the pressure, but ultimately becomes equal to 1/B. By examining the results given in Table III for the higher pressures we see that W_D does not become constant even at the highest temperatures. This merely indicates that 1/B must be considerably greater than 117, the highest value of W_D observed. Or in other words, B must be less and probably much less than 1/117 or 0.008.

5. *Estimation of Ratio E: B.*—According to (39) at low filament temperatures the fraction E/B should be equal to the pressure at which the maximum values of W_D occur. By referring to Table III we see that the highest values of W_D are observed at 50 mm. pressure. At the lower temperatures there is evidence that the maximum should lie at a pressure rather lower than 50 mm., although above 25 mm. The lack of experimental data at intermediate pressures makes it impossible to determine this pressure with much accuracy, but, making allowance for the heating of the gases in the bulb, it is probable that the true pressure at which the maximum W_D would occur is approximately 50 mm. From this we may conclude that E/B = 50.

6. *Most Probable Values of E and* α_1.—Since B must be considerably less than 0.008 and E/B is equal to 50, we may conclude that E must be considerably smaller than 50 × 0.008 or 0.40. We have already seen that E must be greater than $0.0046\sqrt{T_a}$. If we take $T_a = 2500$, E would have to be greater than 0.23. Therefore, E must lie between the comparatively narrow limits 0.23 and 0.40. There is, however, no reason fo

thinking that E must be greater than the lower limit, whereas there is evidence that it is considerably less than the upper limit. The most probable value of E is therefore obtained by placing $\alpha_1 = 1$ in (53). The value thus obtained is, however, almost identical with the value of C given by (46). We have seen from (43) that the mathematical treatment is much simplified if C = E. The small difference between 0.0048 and 0.0046 is well within the experimental error, so that for convenience we may place

$$C = E = 0.0048\sqrt{T_a}. \tag{54}$$

CALCULATION OF K FROM LOW PRESSURE DATA

By the aid of these values of C and E we may calculate K from (43) We have seen that at high temperatures B is less than 0.008. Taking Equation 32 into consideration, we may thus conclude that B must always be less than $0.47/\sqrt{T_a}$. At very low pressures $T_a = 300$, so that under these conditions B might be as large as 0.027. At similarly low pressures E = 0.083. At a pressure P = 0.207 the term BP in (42) is less than 0.005 and may be neglected as compared to E in calculating F. We may thus calculate K from (43) without knowing the value of B, provided we use the data at pressures of 0.207 mm. and lower.

Table IX gives the results of such calculations from the data at the lowest pressures. The values of K were calculated from the corresponding values of W_D by Equation 43, placing F = E. At 0.015 and 0.039 mm. pressure, T_a was placed equal to 300°, but at 0.207 mm. the values of T_a used in the calculation were those given in the next to the last column of the table.

TABLE IX

Dissociation Constant of Hydrogen from Low Pressure Data

	P = 0.015 mm.		P = 0.039 mm.		P = 0.207 mm.		
T.	W_D.	K.	W_D.	K.	W_D.	T_a.	K.
1800	0.007	58×10^{-6}	0.019	165×10^{-6}	0.068	317	501×10^{-6}
1900	0.013	210×10^{-6}	0.05	1.2×10^{-3}	0.15	329	2.1×10^{-3}
2000	0.025	870×10^{-6}	0.09	4.6×10^{-3}	0.27	347	7.5×10^{-3}
2100	0.048	3.9×10^{-3}	0.14	13×10^{-3}	0.45	372	25×10^{-3}
2200	0.085	17×10^{-3}	0.20	34×10^{-3}	0.65	400	64×10^{-3}
2300	0.112	42×10^{-3}	0.27	85×10^{-3}	0.90	430	160×10^{-3}
2400	0.139	112×10^{-3}	0.35	250×10^{-3}	1.17	460	380×10^{-3}
2500	0.169	......	0.40	1.07	1.48	500	1.17
2600	0.179	......	0.45	2.5	1.71	520	2.6
2700	0.180	......	0.47	......	1.84	540	......
2800	0.180	......	0.47	......	1.85	540	......
2900	0.180	......	0.47	......	1.85	540	......

The choice of $T_a = 300$, at the lowest pressures and the tabulated values at 0.207 mm., was based upon calculations similar to those previously employed in obtaining the temperature drop around a wire at low pressures. Thus we may calculate $\varphi_a - \varphi_1$ according to (12), substituting, however, $W_C + W_D$ in place of W_C. The data for the calculation, together with the results, are given in Table X. The values of $W_C + W_D$ were

TABLE X

P.	λ.	S.	$W_C + W_D$ at 2800.	$\varphi_a - \varphi_1$.	$b = 9$ cm. T_a.
0.015	1.3 cm.	5.0	0.19	0.038	321
0.039	0.5	2.8	0.50	0.18	400
0.207	0.1	1.7	1.98	1.19	760
1.1	0.018	1.2	....	.....	...
4.4	0.004	1.0	....	.....	...

taken directly from Table II. In this calculation it is assumed that the hydrogen atoms leaving the filament all recombine to form molecules within a distance λ from the filament and that the heat thus liberated is carried to the bulb by ordinary heat conduction. This assumption, of course, cannot correspond exactly with the facts, but would lead to too high a value for T_a. It is therefore not surprising that the value $T_a = 760$ found at 0.207 mm. should be higher than the value $T_a = 545$ previously calculated by Equation 46 from the data of Table VII. Taking the value $T_a = 545$ as being correct and making a proportionate change in the corresponding values of $\varphi_a - \varphi_1$, we obtain the values of T_a given in Table IX. At the lower pressures the values of T_a are so close to 300° that it is not worth while to take into account the departures from this temperature.

Before discussing the values of K of Table IX, we shall first attempt to calculate K from the data at pressures of 1.1 and 4.4 mm.

At these higher pressures there is more uncertainty as to the value that should be assigned to T_a. We may, however, adopt a method similar to that we employed to calculate T_a at a pressure of 0.207 mm. In the latter case at very high temperatures W_D became independent of T showing that the denominator in Equation 31 was practically zero. This led to Equation 40, from which we determined C and then by (33) we solved for T_a. At the pressures above 0.207 mm., however, W_D does not reach a constant value at the highest temperatures, although it shows a distinct tendency to do so. This is readily seen from Fig. 2, where log W_D has been plotted against $1/T$ for the data at pressures up to 4.4 mm. At the three lower pressures the curve becomes horizontal at the highest temperatures, but at 1.1 mm. the temperatures reached were not high enough to give the maximum value of W_D. From the degree of curvature or the change of slope, we may, however, estimate the value of C and in this way find T_a.

By substituting the value of K from (43) in the modified form of van't Hoff's Equation 50 and carrying out the indicated operations, we obtain (considering F as constant and $T_a = T_2$)

$$\frac{2d \ln W_D}{d(1/T)} + \frac{F\, dW_D/d(1/T)}{P - FW_D} = -\frac{q}{R}. \tag{55}$$

If we let $-U$ be the slope of the curve obtained by plotting $\log W_D$ against $1/T$, then the first term of this equation becomes equal to $-2 \times 2.30\, U$ and in the second term we find $dW_D/d(1/T) = -2.30\, U\, W_D$. Substituting these values in the equation and solving for U we find (since $R = 1.98$)

$$U = \frac{q}{4.57}\left(\frac{P - FW_D}{2P - FW_D}\right) \tag{56}$$

At lower temperatures FW_D becomes negligibly small compared to P, so that U approches a definite limit U_0 which is equal to $0.109\, q$. From this relation we can eliminate q from (56) and then solve for F, with the result:

$$F = \frac{P}{W_D} \cdot \frac{U_0 - U}{U_0 - {}^1/_2 U}. \tag{57}$$

From the curve of Fig. 2 we find the slope of the curve at 2700° ($1/T = 0.000370$) to be 3760. We have already calculated that q is approximately 85000 and from this we obtain $U_0 = 0.109q = 9300$. Substituting these in (57), together with W_D (at 2700°) $= 5.7$ and $P = 1.1$, we obtain

$$F = 0.145.$$

According to (42) $F = BP + E$. The term BP is very small compared to E. We shall see that $B = 0.23/\sqrt{T_a}$ and have already found $E = 0.0048\sqrt{T_a}$. Substituting these values of B, E and F in (42) and solving for T_a, we find $T_a = 810$. From this we may now calculate T_a at all other filament temperatures, as we did at the lower pressures. Thus, taking $S = 1.2$ from Table X, we calculate $\varphi_a - \varphi_1$ from the corresponding values of W in Table II. If we use these values of $\varphi_a - \varphi_1$ we obtain temperatures for T_a that are much too high. However, by empirically taking $0.26\,(\varphi_a - \varphi_1)$ we find, at filament temperature of 2700°, the value $T_a = 810$ in agreement with the calculation above. The values of T_a for other filament temperatures are obtained from the corresponding values of $0.26\,(\varphi_a - \varphi_1)$. The results are recorded in Table XI.

Having thus determined T_a, it is easy to find F at other temperatures by Equations 42, 54 and the relation $B = 0.23/\sqrt{T_a}$. These results are given in the fourth column of Table XI. The values of K given in the fifth column were obtained from F and W_D by (43).

The results shown in Table XII were obtained by exactly similar methods from the data of the experiments at a pressure of 4.4 mm.

TABLE XI

Pressure 1.1 mm.

T_2.	W_D.	T_a.	F.	K.
1800	0.11	350	0.106	0.28×10^{-3}
1900	0.24	360	0.107	1.45×10^{-3}
2000	0.54	390	0.110	7.8×10^{-3}
2100	0.94	430	0.113	25×10^{-3}
2200	1.45	490	0.119	68×10^{-3}
2300	2.22	560	0.125	0.19
2400	3.13	630	0.131	0.47
2500	4.19	720	0.137	1.18
2600	5.00	760	0.141	2.35
2700	5.7	810	0.145	4.7
2800	6.4	840	0.147	10.2
2900	7.0	870	0.149	33.0

TABLE XII

Pressure 4.4 mm.

T_2.	W_D.	T_a.	F.	K.
1800	0.22	370	0.155	0.59×10^{-3}
1900	0.43	390	0.156	2.3×10^{-3}
2000	0.71	420	0.157	6.3×10^{-3}
2100	1.26	460	0.158	20×10^{-3}
2200	2.10	520	0.162	59×10^{-3}
2300	3.42	600	0.166	0.163
2400	4.95	690	0.172	0.38
2500	7.10	790	0.177	0.90
2600	9.80	900	0.183	2.10

FINAL RESULTS FOR THE DISSOCIATION CONSTANT K, AND THE HEAT OF FORMATION q_2

From the experiments at low pressures we have been able to calculate the numerical value of C and E and obtain preliminary estimates of B and *q*. From the experiments at each of the pressures up to 4.4 mm. we have calculated the dissociation constant K at temperatures from 1800 to 2900° and have collected the results in Tables IX, XI and XII.

We are now in a position to test out the correctness of the theory which has been developed in this paper. The conditions which should be fulfilled by the values of K are

1. K should be independent of the pressure.

2. K should vary with the temperature according to van't Hoff's equation; that is, log K plotted against 1/T should give a straight line. The slope of this line determines the value of q.

3. The value of q thus found should agree with that obtained at higher pressures.

We see by examination of the tables that the values of K, found at the three higher pressures 0.207, 1.1 and 4.4 mm. are in excellent agreement. At 0.039 mm. the agreement is also good at the higher temperatures, but poorer at the lower temperatures. The results at 0.015 mm. are considerably lower than the others. On the whole, however, considering that these experiments extend over a range of pressures of nearly 300-fold, the agreement between the different values of K is surprisingly good.

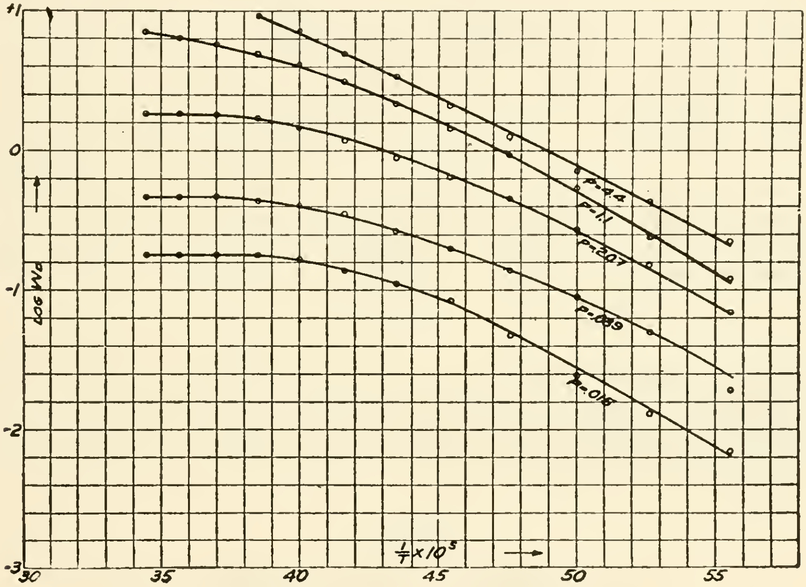

Fig. 2.—Experiments at low pressures.

At the lowest pressures the correction for radiation from the filament is so large that errors from this cause, particularly at the lower temperatures, may perhaps account for the observed variation in K.

In Fig. 3 the values of log K have been plotted against 1/T. In order to prevent the curves from overlapping, the successive curves have been displaced vertically by one unit; thus log K is plotted for P = 0.015 mm., while (1 + log K) has been plotted for P = 0.039 and (2 + log K) for P = 0.207, etc. The curves should be parallel and equidistant straight lines.

The fact that they are actually so very nearly straight and parallel is excellent evidence of the correctness of the theory, especially so, since the curves obtained by plotting W_D in a similar way (see Fig. 2) are by no means straight.

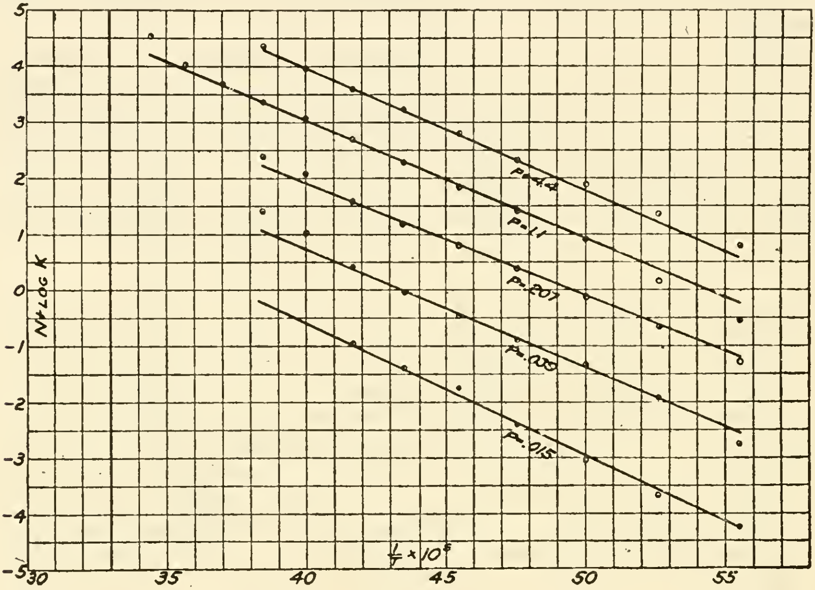

FIG. 3.

Before proceeding further we will now examine the data and choose the most probable values of q to be used in subsequent calculations.

The slope of the lines in Fig. 3 enables us to calculate q by Equation 50. The results thus obtained are given in Table XIII.

TABLE XIII

q = Heat of Formation of Hydrogen at Constant Pressure.

Pressure......	0.015	0.039	0.207	1.1	4.4
q............	108,000	96,000	91,500	100,000	97,000

We may also determine q from the experiments at higher pressures. For this purpose we may combine Equations 50 and 43. The difficulty arises that F is not strictly independent of the temperature, but varies with it slightly and to an extent that depends on the relative magnitude of BP and E (see Equation 42). Since the variation of F with the temperature is small compared with that of W_D, we may proceed as follows in calculating q:

At the higher pressures now being considered, we may safely place $\sqrt{T/T_1} = 1$ in Equation 43. We shall also see that under the conditions of our experiments at higher pressures the term FW_D in the denominator of (43) can be neglected in comparison with P.

Equation 43 thus simplifies to

$$K = F^2W^2_D/P. \tag{58}$$

If we substitute this value of K in (50) and carry out the indicated operations, we obtain

$$\frac{2d \log W_D}{d(1/T)} + \frac{2d \log F}{d(1/T)} = -\frac{q}{4.57} \tag{59}$$

Now it can be readily shown by taking into account Equations 42, 32 and 34 that

$$\frac{2d \log F}{d(1/T)} = \frac{T}{2.30}\,\frac{PB - E}{PB + E}. \tag{60}$$

This term is in the nature of a correction term. The first term of (59) is obtained directly by plotting log W_D against $1/T$. To calculate q we may therefore transform (59) to the following:

$$q = -9.14\,\frac{d \log W_D}{d(1/T)} - 1.98\,T\,\frac{PB - E}{PB + E}. \tag{61}$$

It is seen that the correction term can never exceed 1.98 T.

Curves were prepared from the data of Table III by plotting log W_D against $1/T$. At the higher pressures these curves were very nearly straight lines. The slopes of these lines, multiplied by 9.14, gives the quantities represented by the first term of the second number of Equation 61. The values thus found are given in the second column of Table XIV.

TABLE XIV

Pressure.	$-9.14 \times$ slope.	$-1.98T\,\frac{PB - E}{PB + E}$.	q.
10	+79400	+4000	83400
25	80200	+2000	82200
50	81000	0	81000
100	96200	−2000	94200
200	107600	−3600	104000
750	91400	−5200	86200

To calculate the correction term, the relative values of B and E must be known. We shall see that B is equal to $0.23/\sqrt{T_a}$. If we consider that $T_a = T_2$ and thus calculate B for a mean temperature of 3000, we obtain

$B = 0.005$. Similarly, we find from (54) $E = 0.26$. With these values we may calculate the correction term corresponding to the second term of the second member of (61). The results are shown in the third column of Table XIV.

The resulting values for the heat of formation are given in the fourth column. When these are compared with the values obtained at low pressures (given in Table XIII), it is seen that the agreement is reasonably good.

Averaging all the results gives $q = 93000$. It is felt, however, that a properly weighted mean is closer to 90000. We shall therefore adopt for our final value of q.

$$q = 90000 \text{ calories.} \tag{62}$$

This is the heat of formation of 2 grams of hydrogen molecules from atoms at constant pressure and at 3000° K. At constant volume we obtain (at 3000° K.)

$$q_2 = 84000 \text{ calories.} \tag{63}$$

Substituting the above value for q in (50) and integrating, neglecting the small variation of q with the temperature, we find

$$\log K = a - \frac{90000}{4.57T} = a - \frac{19700}{T}. \tag{64}$$

To determine the coefficient a we need to know the value of K at some one temperature. Let us choose 2300° as the temperature at which the low pressure results for K are most nearly free from experimental error. At higher temperatures the term FW_D in the denominator of (43) introduces some uncertainty, whereas at lower temperatures W_D becomes too small compared with W_C (see Tables II and III). By referring to Tables IX, XI, XII, we thus obtain for $T_2 = 2300$:

Pressure	0.015	0.039	0.207	1.1	4.4
K....	0.042	0.085	0.160	0.193	0.163

The mean of these is $K = 0.12$, but since the results at the lowest pressures are more subject to error a more probable value is thought to be

$$K = 0.16 \text{ at } T_2 = 2300.$$

Substituting this in (64), we find

$$a = 7.77.$$

Our final equation for the dissociation constant of hydrogen is

$$\log K = 7.77 - 19700/T. \tag{65}$$

The values of K corresponding to various values of T as calculated from this equation, are given in the second column of Table XV. From these, the corresponding degree of dissociation at atmospheric pressure and at 1 mm. pressure were calculated by solving the equation:

$$x^2/(1-x) = K/P \tag{66}$$

where x is the degree of dissociation and is equal to

$$x = p_1/P. \tag{67}$$

The results of these calculations are given in the third and fourth columns of Table XV.

TABLE XV

Dissociation Constant K (mm. pressure) and Degree of Dissociation x

		x.				x.	
T.	K.	P = 760 mm.	P = 1 mm.	T.	K.	P = 760 mm.	P = 1 mm.
1200	0.0023×10^{-6}	0.000002	0.00005	2500	0.78	0.0315	0.575
1300	0.042×10^{-6}	0.000007	0.0002	2600	1.55	0.044	0.692
1400	0.48×10^{-6}	0.000025	0.0007	2700	3.0	0.061	0.79
1500	4.3×10^{-6}	0.000075	0.0021	2800	5.4	0.081	0.86
1600	30.0×10^{-6}	0.00020	0.0055	2900	9.3	0.105	0.91
1700	0.00015	0.00044	0.012	3000	16.2	0.13	0.94
1800	0.00066	0.00093	0.025	3100	26.0	0.17	0.96
1900	0.0025	0.0018	0.049	3200	42.0	0.21	0.98
2000	0.0083	0.0033	0.087	3300	63.0	0.25	0.985
2100	0.024	0.0056	0.143	3400	93.0	0.29	0.989
2200	0.065	0.0092	0.224	3500	138	0.34	0.993
2300	0.16	0.0145	0.328	4000	710	0.61	0.999
2400	0.36	0.0216	0.447				

TEST OF THE THEORY

By examining Equations 31 to 34, we see that, by a knowledge of the values of K, q, T_a, B, C, and E, we should be able to calculate W_D for any temperature and pressure. By comparing the results of these calculations with the observations (Table III), we are enabled to test the validity of the assumptions made.

Before making such calculations it is necessary to determine the numerical value of the coefficient B. We have already seen that the maximum value of W_D which we have denoted by $W_{max.}$ is not subject to error through the uncertainty in the actual pressures within the bulb. Equation 44 is therefore particularly well adapted for the calculation of B.

By substituting the values of $W_{max.}$ from Table VIII in Equation 44, together with the corresponding values of K and E and solving the resulting equations for B, the average result is found to be

$$B = 0.23/\sqrt{T_a}. \tag{68}$$

As a test of the theory from which (44) was derived, we may now employ this value of B to calculate $W_{max.}$ and by Equation 45 to calculate P′, using the values of K from Table XV and the values of E given by (54). For these calculations T_a was taken equal to T_2, since the pressures at which W_D reaches a maximum are so high that this must be approximately true. Moreover, the value of $W_{max.}$ is only dependent on T_a to a very slight degree.

TABLE XVI

	$W_{max.}$		P′.	
T.	Calculated.	Observed.	Calculated.	Observed.
2000	1.36	1.4	43	25
2200	3.85	4.0	48	50
2400	8.62	8.9	54	50
2600	17.6	16.7	63	50
2800	30.4	30.0	76	50
3000	48.3	48.0	94	50
3200	69.4	75.0	120	100
3400	92.5	117.0	152	100

The calculated values of $W_{max.}$ and P′ thus obtained are placed in Table XVI side by side with the experimentally found figures.

The agreement in the values of $W_{max.}$ is surprisingly good, especially when it is remembered that the values of K and E, which were used in the calculation, were obtained solely from the experiments at low pressures. The closeness of the agreement over such a wide range of temperature is strong evidence of the correctness of the value of q that was adopted in calculating K.

The discrepancy at the highest temperatures may be explained, I think, as being due to experimental errors caused by electrical leakage through the gas. This effect was noticed strongly at the highest temperatures in the experiment at 4.4 mm. pressure. In this case the discharge through the gas entirely prevented measurements above about 2800°, since the voltage actually decreased as the current was raised. Since the resistance was observed in all cases it was possible to show that this effect was not very serious in the other experiments. It is possible, however, that this effect in an incipient stage may have slightly increased the values of W_D at the highest temperatures, at pressures below 200 mm.

In future experiments this effect could be avoided by using wires of larger diameter so that the potential drop along the wire would be insufficient to ionize the gas.

The agreement between the calculated and observed values of P′ in

Table XVI is also satisfactory. The calculated gradual increase in P′ with increasing temperature is in full accord with the observations.

It must be remembered that the observed pressures were those at which the bulbs were sealed off and that the actual pressures in the bulbs while the filaments were heated must have been much higher. The fact that the calculated values are larger than the observed therefore adds support to the theory.

The value of B obtained above, (68), enables us to calculate the diffusion coefficient D by Equation 32. The shape factor S which is involved in this equation may be calculated from (7), taking $d = 0.00706$ cm. and $b = 3.7$ cm. (see Table V). This gives S = 1.01. By substituting this in (32), together with $q_1 = 42000$ and the value of B from (68), we find

$$D_0 = 9.6 \text{ cm}^2. \text{ per sec.} \tag{69}$$

This is the value of the diffusion coefficient at 0° C. as obtained by extrapolation downwards from high temperatures by Equation 29. At higher temperatures and at atmospheric pressure, we thus obtain from the same equation, together with (69) :

$$D = 2.14 \times 10^{-3}\, T^{3/2} \tag{70}$$

In the "paper of 1912" D was calculated to be equal to

$$D = \frac{0.514 \times 10^{-3}\, T^{3/2}}{1 + 77/T}. \tag{71}$$

This result was obtained, according to the kinetic theory, on the assumption that the free path of hydrogen atoms and hydrogen molecules are the same. At high temperatures the second term in the denominator of (71) becomes negligible and we thus see that the present results show that the diffusion coefficient of hydrogen atoms through molecular hydrogen is 4.2 times as great as had been previously calculated.

A very thorough test of the theory is afforded by a comparison of the values of W_D calculated according to the theory, with those determined experimentally. In Tables XVII and XVIII the observed and calculated values have been placed side by side. The "observed" values are taken directly from Table III of Part I. The calculated values were obtained by solving Equation 43 for W_D after substituting it in the numerical values of K, F, T_a and T_2.

For this purpose the values of K were taken from Table XV, which was obtained directly from Equation 65. At 0.015 and 0.039 mm. pressure T_a was taken to be 300° K., whereas at pressures from 0.207 to 4.4 mm. the

TABLE XVII

COMPARISON OF OBSERVED AND CALCULATED VALUES OF W_D
LOW PRESSURES

	P = 0.015 mm. W_D.		P = 0.039 mm. W_D.		P = 0.207 mm. W_D.		P = 1.1 mm. W_D.		P = 4.4 mm. W_D.	
T_2.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
1800	0.007	0.022	0.019	0.037	0.068	0.083	0.11	0.17	0.22	0.24
2000	0.025	0.066	0.09	0.116	0.27	0.27	0.54	0.58	0.71	0.85
2200	0.085	0.124	0.20	0.25	0.65	0.64	1.45	1.44	2.10	2.31
2400	0.139	0.162	0.35	0.38	1.17	1.12	3.13	2.82	4.95	4.95
2600	0.179	0.176	0.45	0.44	1.71	1.49	5.00	4.4	9.8	9.0
2800	0.180	0.179	0.47	0.46	1.85	1.69	6.4	5.8	....	....

TABLE XVIII

COMPARISON OF OBSERVED AND CALCULATED VALUES OF W_D
HIGHER PRESSURES

	P = 10 mm.		P = 25.		P = 50.		P = 100.		P = 200.		P = 750.	
T_2.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
1800	...	0.31	0.41	0.38	...	0.38	0.33	0.35	0.23	0.28	0.19	0.17
2000	1.0	1.02	1.3	1.3	...	1.35	1.1	1.3	0.67	1.04	0.64	0.62
2200	2.7	2.8	3.2	3.6	4.0	3.8	2.8	3.5	1.70	2.98	1.8	1.8
2400	5.8	6.1	7.1	8.1	8.9	8.7	6.5	8.2	4.0	7.1	4.2	4.4
2600	10.8	11.2	13.5	15.4	16.7	17.2	12.5	16.7	9.0	14.6	8.8	9.2
2800	19.3	17.2	24.0	25.2	30.0	29.7	25.0	30.0	20.0	27.0	17.0	17.3
3000	30.0	23.0	38.6	37.0	48.0	45.5	45.0	48.5	40.0	44.9	29.0	30.0
3200	46.0	26.5	58.0	47.2	74.0	62.0	75.0	69.3	68.0	67.0	47	47.5
3400	....	29.0	.....	54.0	107	75.5	117	90.3	97.0	91.0	69	70.7

values of T_a used in the calculations were those given in Tables IX, XI and XII. At pressures of 10 mm. and more, T_a was taken equal to T_2. The coefficient F was calculated for each temperature and pressure by substituting the values of B and E from (68) and (54) into Equation 42.

The values of W_D have thus been calculated directly from the dissociation constant, the diffusion coefficient, and the coefficients α_1 and α_2. An examination of Tables XVII and XVIII shows that the agreement is on the whole excellent; so good, in fact, that it would seem to show not only that we are dealing with a real dissociation of hydrogen into atoms, but that our theory of the mechanism of the process is substantially correct.

GENERAL DISCUSSION

The theory which has been used in the present paper was only developed after several attempts had been made to calculate the degree of dissociation by other methods. Each of these other methods, however, seemed to lead to conclusions which could only be reconciled with the experimental data by making many improbable and arbitrary assumptions. These difficulties disappear, however, when we adopt the present theory of the mechanism of the reaction. A brief discussion of the unsuccessful hypotheses will enable us to see that they are untenable.

In attempting to analyze the probable mechanism of the reaction, three possibilities suggest themselves:

1. The dissociation occurs in the heated gas around the wire.
2. The dissociation occurs *on the surface* of the wire by the impact of the molecules and atoms against the surface.
3. The dissociation occurs in the wire or in a surface layer where equilibrium prevails.

The first hypothesis assumes that the tungsten does not act catalytically on the reaction, and is therefore in itself very improbable. Moreover, it leads to conclusions irreconcilable with the experiments at low pressures, where, in a sense, there is no heated gas around the wire.

The second hypothesis seemed at first sight to have much in its favor, and by its aid it was possible to estimate an upper and lower limit to the degree of dissociation.

Whatever the mechanism of the reaction on, or in, the wire, it was possible to analyze the process as follows:

Let ε_2 represent, out of all the hydrogen molecules which strike the wire, that fraction which becomes dissociated into atoms. Similarly, ε_1 represents, out of all the atoms that strike the wire, that fraction which recombines to form molecules. We may consider that the reaction actually observed is simply the difference between these opposite reactions. It is clear that neither ε_1 nor ε_2 can ever exceed unity.

For further progress, it is necessary to make some assumptions regarding these coefficients. It is evident that either ε_1 or ε_2 or both must vary with the temperature. The simplest assumption is that they are independent of the pressure. By applying Equation 5 we then readily find that the condition for equilibrium is

$$p_1' = \sqrt{2}\ (\epsilon_2/\epsilon_1)\ p_2'.$$

Since ε_1 cannot exceed unity, this gives us a lower limit for the degree of dissociation, provided we can estimate ε_2. By assuming a value for the heat of reaction it is possible to calculate ε_2 from W_D by an equation similar to (16). In this way it was concluded that the degree of dissociation at 3200° K. and atmospheric pressure must *exceed* 5%.[18]

[18] Table XV gives 21%.

In order, however, to account for the manner in which W_D had been observed to vary with temperature and pressure, it was necessary that ε_2 should increase with the temperature up to a limiting value of 0.68, but at the same time should decrease in a complicated way as the pressure increased. Similarly, ε_1 would have to increase with the pressure and decrease with increasing temperature. This theory gave no clue as to the cause of the variations of ε_1 and ε_2.

The fact that ε_1 and ε_2 were found to be such complicated functions of both temperature and pressure suggested the third hypothesis, namely, that the reaction does not occur at the surface, but that there is an actual equilibrium in the wire which determines the velocity of the reaction. This view was strengthened by the fact that ε_1 and ε_2 varied with the temperature and pressure in the way that would be expected of the partial pressures of two gases in equilibrium.

On the basis of the third hypothesis, the coefficients ε_1 and ε_2 lose their fundamental significance, while the coefficients α_1 and α_2 take their place. The fact that the latter coefficients prove to be constant and practically equal to unity over such wide ranges of temperature and pressure is excellent evidence that, in the present theory, we are dealing with the factors that fundamentally determine the velocity of the reaction.

By means of our present theory we are enabled to calculate ε_1 and ε_2 at any temperature and pressure.

Let us consider the case that hydrogen molecules at pressure p_2 strike the wire, but that the hydrogen atoms formed do not again return to the wire. Then $\varepsilon_2 m_2$ represents the rate of formation of atomic hydrogen. This, however, is equal to the quantity we have called ω (see Equation 17): thus,

$$\omega_2 = \epsilon_2 m_2. \tag{72}$$

Substituting this, together with the value of m_2 (by Equation 5) in (26), we obtain, after placing $\alpha_1 = \sqrt{2}\alpha_2 = 1$

$$K = \sqrt{\frac{T_2}{T_a}}\,\frac{2p_2\epsilon_2^2}{1-\sqrt{2}\,\epsilon_2} \tag{73}$$

This equation shows clearly that at low temperatures, where K is small, ε_2 is inversely proportional to $\sqrt{p_2}$, whereas at higher temperatures it approaches a limiting value of 0.71. Thus the variation of ε_2 with the temperature and pressure which it was necessary to assume when working with the second hypothesis, receives a complete explanation by the third hypothesis.

In a similar way, the value of ε_1 may be calculated for the case that the wire is surrounded by atomic hydrogen, while the partial pressure of molecular hydrogen is zero. In this case

$$\omega_1 = -\epsilon_1 m_i \tag{74}$$

and we thus find, from (26)

$$K = \sqrt{\frac{T_2}{T_g}}\,\frac{(1-\epsilon_1)^2 p_1}{\epsilon_1}. \tag{75}$$

This shows that at low temperatures ε_1 must be constant and equal to unity, whereas at high temperatures it decreases and becomes proportional to the pressure. Thus again, the third hypothesis offers a simple explanation of the difficulty encountered in applying the second hypothesis.

It is evident that ε_1 and ε_2 completely lose their significance when both hydrogen molecules and atoms are present around the wire. We cannot profitably look upon the reaction as being the difference between two opposing reactions taking place *upon the surface.*

In fact, the velocity of the reaction does not follow Gulberg and Waage's Mass Law in the ordinary sense. Neither do diffusion phenomena (at least at low pressures) seem to have any effect on the reaction velocity. The velocity is determined simply by the rate at which the molecules and atoms strike the surface of the wire and the *equilibrium concentrations* of atomic and molecular hydrogen within the wire.

Effect of Bulb Temperature.—In studying chemical reactions at low pressures it has been pointed out [19] that the temperature of the filament and that of the gas molecules striking it can be varied independently of one another. By changing the bulb temperature, the velocity (and internal energy) of the hydrogen molecules striking the filament can be varied over a wide range. If the reaction takes place entirely on the surface in accordance with the second hypothesis, we should expect that the relative velocities of the hydrogen molecules and the tungsten atoms with which they collide, would determine the velocity of the reaction. Because of the small mass of the hydrogen molecules it happens that the average velocity of hydrogen molecules at room temperature or even liquid air temperatures, is much greater than that of tungsten atoms at 3500°. Therefore, the amount of impact between the hydrogen molecules and tungsten atoms depends vastly more on the bulb temperature than it does on the temperature of the filament. In case the impact determines the reaction velocity, we see that the latter should be greatly affected by bulb temperature.

On the other hand, if the reaction takes place in the metal in accord

[19] Langmuir, *Jour. Amer. Chem. Soc., 35,* 105 (1913).

with the third hypothesis, we should not expect the bulb temperature to materially affect the velocity of the reaction. It is to be expected, however, that the bulb temperature might have a slight effect on the coefficient α_2 and thus slightly change the velocity of the reaction.

Some experiments were undertaken to determine whether cooling the bulb in liquid air had any effect on the values of W_D obtained at low pressures (from 0.01 to 0.1 mm.). The results showed conclusively that the bulb temperature was without material effect on the velocity of the reaction. This fact affords additional evidence that the velocity depends primarily on some equilibrium condition within the surface of the wire.

Specific Heat of Hydrogen at High Temperatures.—When hydrogen is heated to a temperature at which appreciable dissociation occurs, the heat absorbed by the reaction may be very large compared with that which would be required if there were no dissociation. We should therefore expect a very large increase in the apparent specific heat of hydrogen at very high temperatures. In Part I we have already briefly discussed Pier and Bjerrum's experiments on the specific heat of hydrogen by the explosion method. We saw that the earlier calculations of the dissociation of hydrogen (paper of 1912) led to apparent specific heats too high to reconcile with the results of the explosion method, unless we assumed that equilibrium was not reached during the short period of the explosion.

In order to compare our present results with the data of the explosion method, we shall calculate the increase in apparent specific heat caused by the dissociation as given in Table XV.

If we heat a gram molecule of hydrogen from 0° K. to T, the number of gram molecules of hydrogen dissociated will be $x/(2-x)$ where x is the degree of dissociation at the temperature T, x being expressed in terms of partial pressures according to (67).

The heat absorbed by this dissociation will be

$$q_2 x/(1-x).$$

In comparison with this we may neglect the increase in specific heat due to the difference in the specific heat of the molecular hydrogen and that of the atomic hydrogen formed (2×2.98).

Pier [20] gives for the *mean* specific heat of hydrogen from room temperature up to $t°$ C.

$$C_v = 4.70 + 0.00045t$$

or in absolute temperatures

$$C_v = 4.578 + 0.00045T$$

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[20] *Z. Elektrochem.*, *15*, 536 (1909).

The dissociation at higher temperatures would cause an increase in this mean specific heat amounting to

$$\frac{q_2}{T-273} \cdot \frac{x}{(2-x)}.$$

In Table XIX are given the mean specific heats for a few temperatures, as calculated from Pier's formula, together with those calculated by taking into account the increase due to dissociation. For this calculation the values of x were taken from Table XV and q_2 was taken to be 8400 calories.

TABLE XIX

T.	C_v. Pier.	Apparent C_v (considering dissociation).	Ratio.
1600	5.30	5.306	1.0012
1800	5.39	5.41	1.0047
2000	5.48	5.56	1.015
2200	5.57	5.77	1.036
2400	5.66	6.09	1.078
2600	5.75	6.56	1.14
2800	5.84	7.25	1.24
3000	5.93	8.09	1.36
		9.40	1.56

Siegel, in a recent paper,[21] discusses in detail the errors of the explosion method. He points out that, owing to a faulty method of calculation, the temperatures given by Bjerrum are considerably too high, in some cases as much as 400°. He then shows that Bjerrum's experiments exhibit certain discrepancies which could be readily explained by assuming a dissociation of the hydrogen. He then says (pages 649–50):

> "In order to reconcile Langmuir's results with those of the explosion method, one must assume that in the calculations thus far, the capacity of the system (in the explosion chamber), that is, $C_{H_2O} + MC_{H_2}$, has been taken about 30% too high.
>
> "Such an assumption . . . is impossible. However, if we take for the heat of dissociation of hydrogen, the value 140000 calories instead of the 131000 calories given by Langmuir, we then find by the Nernst approximation formula:
>
> $$\log K = Q/4.57\,T + \Sigma v . 1.75 \log T + \Sigma v C$$
>
> that at 2850° and atmospheric pressure the dissociation is about 11%, which is the value given by Langmuir for 2700°. With this assumption it can be shown that the heat capacity of the system at 2850° would be 13% less than previously taken. This result is no longer irreconcilable with the other results of the explosion method. However, I am of the opinion that the heat of dissociation of hydrogen should be at least

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[21] *Z. phys. Chem.*, *87*, 641 (1914).

> 150000 calories. On the other hand, it should be emphasized that from my experiments it is not possible to determine with certainty whether or not hydrogen is dissociated at all. And—what is here very significant—by the assumption of such a dissociation, the observed anomalies in the heat losses do not find a sufficient explanation, for the anomalies also occur even at temperatures as low as 2300–2400°, where surely the dissociation of hydrogen can play no part."

Thus, according to Siegel, a dissociation as large as 11% at 2850° can be reconciled with the explosion experiments. If we refer to Table XV we see that we have found the dissociation at 2850° to be 9.2% at atmospheric pressure. This should be ample to account for the anomalies found by Siegel.

Siegel's objection that the dissociation of hydrogen could not account for the discrepancies observed at 2300–2400°, fails to apply to the present results. Siegel does not state his reasons for believing that the heat of dissociation is at least 150000 calories. Such a high value is at complete variance with all the experiments described in the present paper. With the value 84000 calories which we have adopted, the dissociation does not fall off nearly so rapidly at lower temperatures. This is readily seen from the following table:

	Siegel. $q = 150000$.		Langmuir. $q = 84000$.	
T.	**x.**	**$\Delta C/C$.**	**x.**	**$\Delta C/C$.**
2850	**0.11**	**13.0%**	**0.092**	**11.0%**
2300	**0.0049**	**0.9%**	**0.014**	**2.6%**

The figures in the second column represent the degree of dissociation calculated from Siegel's data, while those in the fourth column are taken from Table XV. The third and fifth columns give the increase in the "heat capacity of the system" $H_2O + MH_2$ referred to by Siegel. Thus, Siegel calculates that 11% dissociation at 2850° would increase the capacity by 13%. The other figures were obtained from this by proportion, taking into account, however, the effect of the temperature as was done in the preparation of Table XIX.

Thus, on Siegel's assumption of a high heat of dissociation, the effect of the dissociation is to increase the heat capacity at 2850° by 13%, but only by 0.9% at 2300°. It is evidently for this reason that he says that "surely the dissociation can play no part" at such low temperatures as 2300°.

Taking the values for the dissociation as calculated in the present paper, we find that the heat capacity would be increased 11% at 2850 and 2.6%

at 2300°, an amount probably sufficient to account for the anomalies found by Siegel.

Thus, the explosion method gives additional evidence for the dissociation of hydrogen and confirms the substantial accuracy of the results.

RATE OF FORMATION OF ACTIVE HYDROGEN

It has been shown[22] that the disappearance of hydrogen in contact with a heated filament is caused by the deposition of atomic hydrogen on the bulb.

The present theory enables us to calculate the rate at which atomic hydrogen should be formed in contact with a tungsten wire. The rate at which atomic hydrogen is deposited on the bulb should naturally be less than that at which it is formed by the wire.

In the paper referred to, it was stated that the disappearance of hydrogen "was often quite marked when the wire was at a temperature as low as 1300° K.," but very few quantitative data at such low temperatures were given. By looking through the original notes of these experiments, I find that at low temperatures the highest rates of disappearance were as follows:

Experiment 160. Filament temperature 1200° K. In seven minutes the pressure fell from 16.4 to 15.6 microns, although at 1100° K. no decrease in pressure could be observed. The surface of the filament was 0.15 sq. cm. The rate of disappearance was 1.4 cubic millimeters of H_2 per minute per sq. cm. of surface.

Experiment 173. With the filament at 1270° the pressure decreased from 16.2 to 15.0 microns in three minutes. The surface of the filament was the same as before. This corresponds to a rate of 3.7 cubic mm. per minute per sq. cm.

In each case the hydrogen continued to disappear at a gradually decreasing rate for a half-hour or more. Because of this fatigue effect we shall here consider only the initial rates.

Let us now calculate the rate at which atomic hydrogen should have been produced by wires at these temperatures. In Equation 26 we may place $p_1 = 0$; $p_2 = P$ and may neglect the second term of the denominator at these low pressures and temperatures. Since the factor $\sqrt{2\pi R}$ is equal to 17.15 and α_1 is unity, we thus obtain

$$K = 325.\sqrt{T_a T_1}\,\omega^2/P. \qquad (76)$$

In this equation ω is the rate of dissociation of hydrogen in grams per second per sq. cm. of filament surface. Let R be the rate of dissociation of molecular hydrogen in cubic mm. per sq. cm. per minute. We then have

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[22] *Jour. Amer. Chem. Soc., 34,* 1310 (1912).

$$R = 7.2 \times 10^8 \omega \tag{77}$$

whence from (76), by placing $T_a = 300$

$$R = 9.6 \times 10^6 \sqrt{KP}\, T^{-1/4}. \tag{78}$$

Substituting in this the values of K from Table XV and taking the values of P and T given above, we obtain the values given below as "R cal." For comparison these are placed side by side with those found by experiment.

	T.	R calc.	R obs.
Expt. 160	1200	9.8	1.4
Expt. 173	1270	27.4	3.7

These results indicate that under the most favorable conditions realized in the experiment, only about one-seventh of the hydrogen dissociated was deposited as "active hydrogen" on the bulb. In the great majority of cases the fatigue effect made the observed rate of clean-up much slower.

The fact that the observed rates are less than the calculated, yet of the same order of magnitude, is a satisfactory confirmation of the theory that the disappearance and activation of hydrogen are caused by its dissociation into atoms.

There is thus quantitative evidence of the dissociation of hydrogen over the whole range of temperature from 1200° to 3500°. The substantial agreement of the calculated and observed results over such a wide range proves that the value we have found for the heat of dissociation, namely, 84000 calories, cannot be far from correct.[23]

EXPERIMENTS WITH MIXTURES OF HYDROGEN AND NITROGEN

Some experiments have been made to determine the heat losses from tungsten wires in mixtures of nitrogen and hydrogen. The wire was the same as that previously used in the experiments with hydrogen. The bulbs, after being exhausted in the usual way, were filled with the mixture of gases, the *total* pressure in each case being 600 mm. Mixtures containing 1.25, 3.0, 10.0 and 30% of hydrogen were used. The results given in Table XX were obtained by subtracting from the observed watts per centimeter, the energy radiated (W_R). These figures are directly comparable with those given in Table I of Part I.

To obtain the heat carried from the wire by the dissociation, it is

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[23] For example, it now becomes impossible to reconcile our experiments with the value $q_2 =$ 63000 calculated according to the method of Bohr, *Phil. Mag., 26,* 863 (1913); *27,* 188 (1914).

TABLE XX

Diam. of wire 0.00706 cm. Total pressure 600 mm.

T.	W_R.	Watts per cm. carried by mixture.				W_C in N_2. S = 1.36.	W_C in H_2. S = 1.18.
		p_o = 7.5 mm.	p_o = 18 mm.	p_o = 60 mm.	p_o = 180 mm.		
1800	0.38	1.45	1.52	2.06	....	1.40	7.4
2000	0.65	1.75	1.85	2.40	....	1.70	9.0
2200	1.06	2.10	2.30	2.86	4.5	2.02	10.7
2400	1.60	2.60	2.95	3.70	5.8	2.36	12.6
2600	2.33	3.35	3.70	4.92	7.9	2.75	14.5
2800	3.30	4.23	4.70	6.78	11.4	3.14	16.8
3000	4.46	5.15	6.20	9.30	....	3.58	19.1

TABLE XXI

Observed and Calculated Values of W_D

T.	p_o = 7.5 mm.		p_o = 18 mm.		p_o = 60 mm.		p_o = 180 mm.	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
1800	−0.01	....	−0.03	....	+0.08	....	...	...
2000	+0.06	0.03	−0.05	0.04	0.00	0.08	...	...
2200	0.00	0.08	+0.05	0.13	0.00	0.24	−0.1	0.4
2400	+0.25	0.20	+0.33	0.32	0.36	0.60	+0.4	1.0
2600	0.45	0.41	0.60	0.65	1.00	1.23	1.6	2.2
2800	0.93	0.72	1.18	1.20	2.30	2.30	4.2	4.2
3000	1.37	1.10	2.20	1.92	4.18	3.96	...	...

necessary to substract W_C. In the last two columns of Table XX are the calculated values of W_C for pure nitrogen and hydrogen at pressures of 600 mm. These are obtained by multiplying S by the values of $\varphi_2 - \varphi_1$ given in Tables III and IV. For the mixture of hydrogen and nitrogen W_C was found by interpolating linearly between the values calculated for the pure gases. By subtracting these results from the watts per cm. of Table XX the values of W_D given in Table XXI as "cal." were obtained. The smallness of the differences at lower temperatures shows that the heat carried by convection in mixtures of gases is approximately an additive function of the partial pressures (the total pressure remaining constant).

To calculate the values of W_D for mixtures of gases according to our theory we need to start from Equation 27. From this we can eliminate p_1 and p_2 as bfore, by means of Equation 30. The significance of P and p_2, however, is now somewhat different, as we must proceed from this point in a slightly different way. In Equation 30, P is the total pressure, and p_1 the partial pressure of atomic hydrogen. We then have

$$p_2 = p_o - {}^1/_2 p_1 \qquad (79)$$

where p_o is the partial pressure of molecular hydrogen before dissociation occurs and p_2 is the partial pressure of molecular hydrogen after dissociation.

In the present case we may place $T_a = T_2$; $P = 600$, $S = 1.34$, and $q_1 = 42000$. From (30) we thus find

$$p_1 = 946 W_D/(D_0 \sqrt{T}). \qquad (80)$$

Combining (79) and (80) with (27), we find

$$K = \frac{W^2_D\,(946/D_0\sqrt{T} + E)^2}{p_0 - W_D\,(473/D_0\sqrt{T} + E)} \qquad (81)$$

where E is given by (34).

By trial it was found that (81) gives the best agreement between the observed and calculated values of W_D if D_0 is placed equal to 2.5.

Calculating E by (54) it is evident that E is negligible compared to $473/2.5\sqrt{T}$ over the whole range of temperatures covered by the experiments. Equation 81 thus simplifies to

$$W_D = \sqrt{\frac{Kp_0T}{144000}} \times \sqrt{1 - \frac{190}{p_0\sqrt{T}}\,W_D}. \qquad (82)$$

This quadratic equation can be conveniently solved for W_D by using a series of approximations, since the second radical is always close to unity. In this way, by taking K from Table XV, the values of W_D for different temperatures and partial pressures have been calculated. The results are placed side by side with the observed values in Table XXI.

The agreement is entirely satisfactory, considering the crudeness of some of the assumptions made.

The theory receives additional confirmation through the fact that the observed values of W_D increase in proportion to the square root of the partial pressure as demanded by the theory, whereas at lower temperatures the observed values of W_C increase linearly with the partial pressure.

From the value of D_0 we may conclude by (29) that the diffusion coefficient of hydrogen atoms through nitrogen at high temperatures and atmospheric pressure is

$$D = 2.5\,(T_a/273)^{3/2}. \qquad (83)$$

Comparing this with (69) we see that the ratio of the diffusion coefficient of hydrogen atoms through hydrogen to that through nitrogen is $9.6/2.5 = 3.84$.

If we calculate the free path of hydrogen atoms through nitrogen according to the principles of the kinetic theory, using Equations 20 and 21 on page 865 of the "paper of 1912," we obtain

$$D_{\text{cal.}} = 2.16\,(T/273)^{3/2}. \qquad (84)$$

This agrees well with the diffusion coefficient calculated from the experiments (Equation 83). We have previously remarked that the observed rate of diffusion of hydrogen atoms through molecular hydrogen was found to be 4.2 times greater than that calculated. Evidently hydrogen atoms behave abnormally when diffusing through molecular hydrogen, but not when diffusing through nitrogen. This is probably caused by the hydrogen atoms going, we might say, through the hydrogen molecules by combining with one atom in a molecule with which it collides and thus liberating the other. This effect is probably entirely analogous to the abnormal mobility of the H and OH ions in aqueous solutions.

SUMMARY

1. Previous calculations of the degree of dissociation of hydrogen, from experiments on the heat losses from tungsten wires in hydrogen, conflicted rather seriously with Bjerrum's determinations of the specific heat of hydrogen by the explosion method. The weak point in the method of calculation was a rather arbitrary assumption regarding the diffusion coefficient of atomic hydrogen through ordinary hydrogen.

2. This apparent discrepancy suggested that the actual amount of dissociation might be somewhat less than that previously calculated, but did not indicate that the abnormal heat conductivity of hydrogen at high temperatures was not due to dissociation.

3. The qualitative evidence of such a dissociation seems conclusive. Thus, not only does hydrogen show an entirely abnormal increase in heat conductivity, but this heat conductivity actually increases as the pressure is lowered.

A large amount of chemical evidence has also been accumulated. If hydrogen at low pressures comes into contact with metallic wires at temperatures above 1300° K., part of the hydrogen is converted into an active modification which remains adsorbed on glass surfaces for long periods of time. This active hydrogen can react at room temperature with oxygen or with many reducible substances, or can dissolve in metals such as platinum. There are good reasons for thinking that this active hydrogen is hydrogen in the atomic condition.

4. A series of experiments were made to measure, more accurately than hitherto, the heat losses from a tungsten wire at temperatures from 800° to 3500° K. and at pressures of hydrogen ranging from 0.01 mm. up to atmospheric pressure. Similar experiments were made with nitrogen.

5. At temperatures below that at which dissociation occurs the heat loss from the wires decreases steadily as the pressure is lowered. Only at pressures above 200 mm. do convection currents play any important part.

Below this pressure the decrease in the heat loss is due to the temperature discontinuity, first observed by Smoluchowski. The theory of this effect is developed for the case of small wires at very high temperatures and the results are found to be in good agreement with the experiments.

6. The normal heat conductivity is separated from the abnormal effect due to dissociation, and a table is prepared (Table III) giving the heat carried from the wire by the dissociation, at various temperatures and pressures. With nitrogen there is no abnormal increase in heat loss at high temperatures.

7. The following theory of the phenomena occurring in and around the wire is proposed:

The dissociation of the hydrogen does not occur in the space around the wire, nor by the impact of molecules against its surface, but takes place only among the hydrogen molecules which have been absorbed (dissolved?) by the metal of the wire. Within the metal the reaction occurs so rapidly that equilibrium may be assumed to prevail at all times.

The equilibrium constant within the metal may, however, be very different from that in the gas phase.

It is assumed that there is no "adsorption film" on the surface of the wire through which the hydrogen has to diffuse, but that the absorption takes place by the collision of the molecules (or atoms) against the surface of the wire. A certain proportion of the molecules striking the surface may be reflected without absorption. Thus, of all the hydrogen molecules striking against the surface, we assume that a certain fraction α_2 is absorbed, while the fraction $1 - \alpha_2$ is reflected. Similarly, of all the hydrogen atoms striking the surface, the fraction α_1 is absorbed.

In general, the partial pressures of atomic hydrogen in the gas immediately surrounding the wire will not be that corresponding to the equilibrium at the temperature of the wire. The difference between these two partial pressures may be looked upon as a "drop in concentration" at the surface of the wire strictly analogous to Smoluchowski's "temperature drop" in the case of heat conduction and to Kundt and Warburg's "slip" in the case of experiments on the viscosity of gases.

The partial pressure of atomic hydrogen immediately around the wire depends on: 1st, the rate at which atomic hydrogen escapes from the wire; 2nd, the rate at which atomic hydrogen is absorbed by the wire; and 3rd, the rate at which it can diffuse away from the wire.

8. From the viewpoint of this theory it has been possible, by thermodynamical reasoning, to develop a quantitative theory by which the dissociation constant K (in the gas phase) may be calculated in terms of W_D the heat carried from the filament by dissociation; q_1 the heat of reaction; D the diffusion coefficient, and the two coefficients α_1 and α_2.

The resulting general Equation 31 is of the form (neglecting constant factors)

$$K = \frac{(W/q)^2 \, (P/D + 1/\alpha_1)^2}{P - (W/q) \, (P/D + 1/\alpha_2)}$$

where P is the total pressure.

9. By comparing this equation with the experimental data, it is found possible to so choose the quantities K, q, D, α_1 and α_2 that the resulting equation agrees excellently with the experiments at all temperatures and pressures. At the same time, the values of K conform to the thermodynamical requirement given by van't Hoff's equation

$$d \ln K/dT = q/RT^2.$$

The agreement between the theory and the experiments is shown in Tables XVII and XVIII, where the observed and calculated values of W are placed side by side.

10. The values of the quantities K, q, D, α_1 and α_2 which were used in these calculations, and which were found to give the best agreement between experiment and theory, are as follows:

Dissociation Constant K.—Let us define the dissociation constant K by the equation:

$$K = p_1^2/p_2 \tag{22}$$

p_1 and p_2 being the partial pressures (in mm.) of atomic and molecular hydrogen, respectively. Then it is found that

$$\log_{10} K = 7.77 - 19700/T. \tag{65}$$

Values of K calculated from this equation for temperatures from 1200 to 4000° have been given in Table XV, together with the corresponding degrees of dissociation at pressures of 760 mm. and 1 mm. The following is a comparison of these results with those obtained previously (in the year 1912):

Degree of Dissociation at 760 mm.

Temp. ° K.	2000	2300	2500	3100	3500
Results in 1912	0.0013	0.012	0.039	0.44	0.84
Results in 1915	0.0033	0.014	0.031	0.17	0.[illegible]4

In the range from 2200–2600°, the results are nearly identical, but at higher and lower temperatures the differences become large.

Heat of Formation of Hydrogen Molecules.—By applying van't Hoff's equation to the foregoing data, we find the heat of reaction for two grams of hydrogen to be

84000 calories at constant volume
90000 calories at constant pressure

In 1912 the value given was 130000 calories at constant volume.

Diffusion Coefficient of Atomic Hydrogen in Molecular Hydrogen.—This quantity is found to be

$$D = 2.14\ 10^{-3}\ T^{3/2}. \qquad (70)$$

This result is 4.2 times greater than that found previously by calculation from the principles of the kinetic theory. This difference suggests that the hydrogen molecules are more or less "transparent" to hydrogen atoms. The effect is probably quite analogous to that of the abnormal mobility of the H and OH ions in aqueous solutions.

The Coefficients α_1 *and* α_2.—The coefficient α_1 is found to be constant and equal to unity, while α_2 is apparently constant and equal to 0.68. In other words, *all the hydrogen atoms striking the filament are absorbed by it and 68% of all the hydrogen molecules are absorbed.* The velocity of the reaction is thus determined practically entirely by the equilibrium conditions within the wire. The fact that these coefficients are found to be so nearly equal to unity is excellent evidence that in the present theory we are actually dealing with the fundamental factors determining the velocity of the reaction.

11. Other possible theories of the mechanism of the reaction are discussed, but no other is found which agrees at all well with the facts.

12. The apparent increase in specific heat caused by the dissociation is calculated. Even at temperatures as low as 2000° the effect should be perceptible. The magnitude of the effects found is, according to statements of Seigel, of the right order to account fully for certain anomalies in the experiments of Bjerrum. Therefore, the results of the explosion method, instead of conflicting with the present determinations of the degree of dissociation, may be regarded as additional evidence in their favor.

13. The rate at which hydrogen at very low pressures is dissociated by a tungsten wire at 1200–1500° has been calculated according to the theory and is found to be 8–10 times greater than the *greatest* observed rate at which active hydrogen was deposited on glass surfaces. In view of the marked fatigue effects characteristic of this adsorption of active hydrogen by glass, the agreement is close enough to lend further support to the theory. The quantitative evidence of the dissociation of hydrogen may therefore be said to extend over a temperature range from 1200 to 3500° K., in which the degree of dissociation increases in the ratio 1 : 170000.

14. Experiments on the heat losses from tungsten wires in mixtures of nitrogen and hydrogen yield results also in accord with the theory. See

Table XXI. The diffusion coefficient of hydrogen atoms through nitrogen is found to be

$$D = 2.5\ (T/273)^{3/2}$$

which is in excellent agreement with a value calculated by the kinetic theory.

PART THREE

THE DISSOCIATION OF HYDROGEN INTO ATOMS

THE MECHANISM OF THE REACTION

In part II of this paper [1] the degree of dissociation of hydrogen into atoms has been calculated from data [2] on the heat losses from highly heated wires in hydrogen at various pressures. In this calculation it was necessary to make certain assumptions regarding the mechanism of the processes occurring on and around the wire. The remarkable agreement between the theory thus derived and the experimental results, furnished ample justification for the assumptions, but did not necessarily indicate that the particular mechanism assumed was the only one which would lead to similar agreement.

The writer has recently developed a theory [3] of heterogeneous reactions which throws a great deal of light on the mechanism of such reactions. Applied to the dissociation of hydrogen around a heated wire, this theory leads to a mechanism which may seem radically different from that previously used, but curiously enough it results in an equation identical with that obtained by the original theory.

The object of the present paper is to compare the older and the newer theories and to point out the advantages of the latter. At the same time this will serve as an illustration of the principles of the new theory and will indicate how it may be of use in the study of other heterogeneous reactions.

In the theory previously described, it was assumed that the surface of the tungsten wire contained atoms and molecules of hydrogen in chemical equilibrium with each other. The atomic and molecular hydrogen escaped from the wire at rates respectively proportional to their concentrations in the wire, while the absorption of the atoms or molecules by the wire was taken to be proportional to the corresponding pressures in the gaseous phase.

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[1] *Jour. Amer. Chem. Soc., 37,* 417 (1915).

[2] Part I, Langmuir and MacKay, *Jour. Amer. Chem. Soc., 36,* 1708 (1914).

[3] This theory has, as yet, been only very briefly described (*Jour. Amer. Chem. Soc., 38,* 1139 (1915) and *Jour. Ind. Eng. Chem., 7,* 348 (1915); *Phys. Rev., 6,* 79 (1915)), but will serve as the basis of a series of papers to appear in *Jour. Amer. Chem. Soc.* and in the *Phys. Rev.*

This theory led to an equation for the heat loss from the wire which proved to be in excellent agreement with experiments extending over a range of pressures from 0.01 mm. up to 760 mm. and a range of temperatures from 1000 to 3500° K. There are, however, some serious objections that may be raised against the assumption that the wire contains *concentrations* of atomic and molecular hydrogen in equilibrium with each other, and that these concentrations determine the rate at which hydrogen is dissociated by the wire. We shall see, however, that the new theory enables us to derive the same equation without making these objectionable assumptions.

The hypothesis that solid solutions of gases in metals play an important role in chemical reactions in contact with metals is a common one, and usually is not looked upon unfavorably. But it is evident that if we are to retain our ordinary conception of *concentration* the reaction must take place in a volume which contains many layers of atoms. In the experiments the range of concentrations of molecular (or atomic) hydrogen in the metal phase must have been enormous. Thus under some of the experimental conditions the concentrations were so small that the individual atoms or molecules of hydrogen were certainly separated from each other by hundreds of tungsten atoms. The rapidity of the reaction under such conditions could not possibly be very high and would be limited by the rate of diffusion of the gas through the metal.

Yet the experiments showed clearly that the velocity with which equilibrium was reached on the surface was extraordinarily high under all conditions. In fact, it was so high that practically all of the hydrogen atoms and 68% of the molecules which struck the surface reached equilibrium before leaving it again. When we consider that at atmospheric pressure and room temperature 1.1×10^{24} molecules of hydrogen strike each square centimeter of surface per second, and that this number of molecules is contained in about 44 liters of gas, we realize the enormous velocity which this reaction must have. It is certainly impossible that such amounts of gas per second could diffuse *into* any kind of solid body and thus be brought to equilibrium.

These considerations compel us to assume that the reaction occurs directly on the surface of the metal and that it does not involve the diffusion through a film even as thin as that of a single layer of atoms.

A second difficulty arose in connection with the original theory.

At temperatures up to about 1500° K. the accommodation coefficient of hydrogen in contact with tungsten was found to be equal to 0.19. In other words, only about 19% of all the hydrogen molecules striking the filament, reached *thermal* equilibrium with it before leaving it. This figure was in good accord with the value 0.26 obtained by Knudsen with platinum at room temperature, especially when the fact was taken into account that accommodation coefficients in general appear to have slight negative temperature coefficients.

On the other hand, at high temperatures, it was found that 68% of all the hydrogen molecules striking the filament reached *chemical* equilibrium before leaving it. The original theory gave no clue to the solution of the paradox that 68% of the molecules reached chemical equilibrium, while only 19% reached thermal equilibrium. It is certainly impossible that molecules should reach chemical equilibrium while great differences in temperature still persist.

The viewpoint which has served as the basis for the new theory was gradually developed in quite other lines of work, particularly in connection with a study of the effect of gases on the electron emission from heated metals.[4] It was found that the electron emission was dependent on the composition of the actual surface layer of atoms. The deeper layers were apparently without effect. Subsequent work on gas reactions at very low pressures [5] indicated clearly that chemical reactions between a gas and a solid depend in general on the composition or structure of the outside layer of atoms of the solid, rather than on the thickness of an adsorbed film through which the gases diffuse.

This theory has now been developed much more completely than in any of the previously published work.

It is definitely known from the work of Bragg and others that the atoms of crystals are arranged according to space lattices in such a way that the identity of molecules is usually lost. The forces holding the crystal together are thus clearly chemical forces which act probably only between adjacent atoms. On the surface of a crystal the forces tend to be chemically unsaturated, and atoms or molecules of gases can thus be held firmly by the atoms of the solid.[6] In general the law of multiple combining proportions will apply. Thus each metal atom of the surface will be capable of holding a definite integral number (such as one or two) of atoms of the gas, or possibly each two atoms of metal may hold one atom of gas. The atoms held on the surface in this way will form a part of the solid body, being a real continuation of the space lattice of the solid. This layer of atoms (or molecules) on the surface may be said to be adsorbed.

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[4] Langmuir, *Phys. Rev.*, *2*, 450 (1913) ; *Physik. Z.*, *15*, 516 (1914).

[5] *Jour. Amer. Chem. Soc.*, *37*, 1139 (1915).

[6] Haber (*Jour. Soc. Chem. Ind.*, *33*, 50 (1914) and *Z. Elektrochem.*, *20*, 521 (1914)) has suggested on the basis of Bragg's theory, that adsorption may be the result of unsaturated chemical forces at the surface of a solid body. Haber, however, only considers the force causing adsorption and does not take into account that the amount of adsorption depends on a kinetic equilibrium between the condensation and the evaporation of molecules.

The surface of the metal is thus looked upon as a sort of checkerboard containing a definite number, N_0 of spaces per square cm. Each elementary space is capable of holding an atom or a definite part of a molecule of adsorbed gas. The number of elementary spaces, N_0, is probably usually equal to the number of metal atoms on the surface. But this is not essential, for we can imagine cases in which each metal atom holds, for example, two adsorbed atoms or molecules, so that we should then have twice as many elementary spaces as metal atoms on the surface.

Let us now apply this theory to the dissociation of hydrogen in contact with a heated tungsten wire. We will first calculate the rate at which atomic hydrogen condenses on the bare surface when atomic hydrogen at a pressure p surrounds the wire.

The number of grams of gas which strikes a sq. cm. of surface per second is

$$m = \sqrt{\frac{M}{2\pi RT}}\, p. \qquad (1)$$

Let μ represent the number of gram molecules of gas striking a sq. cm. per second. Then $\mu = m/M$ or

$$\mu = \frac{p}{\sqrt{2\pi MRT}}. \qquad (2)$$

Expressing p in bars,[7] and placing $R = 83.15 \times 10^6$ ergs per degree, this reduces to

$$\mu = 43.75 \times 10^{-6} \frac{p}{\sqrt{MT}}. \qquad (3)$$

By applying this equation, we can readily calculate the rate at which atomic hydrogen ($M = 1$) comes into contact with each square centimeter of surface. The rate at which the gas condenses to form a layer (one atom deep) on the surface will be less than the rate at which it strikes the surface for two reasons. In the first place, only a fraction α of the atoms which strike the bare surface condenses, while the fraction $1 - \alpha$ is reflected. Secondly, as the surface becomes covered with hydrogen atoms, many atoms will strike portions of the surface already covered.[8]

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[7] The bar is the C. G. S. unit of pressure, one dyne per sq. cm. One million bars or one megabar is equal to 750 mm. of mercury, which is more nearly average atmospheric pressure than the 760 mm. usually used.

[8] There is good reason to believe that even the hydrogen atoms which strike a surface already covered condense. But the rate of evaporation of the atoms from such a surface is so much higher than that from a bare surface that the number of atoms in the second layer is probably negligible in comparison with that in the first.

Let θ represent the ratio of the number of vacant elementary spaces to the total number of spaces N_0. Thus θ is the fraction of the surface which is bare. The rate at which atomic hydrogen condenses on the surface is thus equal to $\alpha\theta\mu$.

Consider the case of hydrogen molecules condensing on the surface. If each hydrogen molecule occupies only one elementary space, then the rate of condensation will still be given by the product [9] $\alpha\theta\mu$.

If, on the other hand, each hydrogen molecule should occupy two elementary spaces, then the rate at which molecular hydrogen would condense on the surface is equal to $\alpha\theta^2\mu$. The exponent 2 for the quantity θ is due to the fact that two adjacent spaces must be vacant simultaneously, in order that the molecule may condense. The chance that a given space, towards which a gas molecule may be moving, shall be vacant, is θ. The chance that two given spaces shall be simultaneously vacant is θ^2.

The adsorbed atoms or molecules on the surface evaporate at a definite rate. Let the rate of evaporation in gram molecules per sq. cm. per second from a completely covered surface, be represented by ν. If θ_1 is the fraction of the surface which is covered by the atoms or molecules in question, then the actual rate at which the hydrogen evaporates is $\nu\theta_1$.

In considering the mechanism of the dissociation of hydrogen in contact with a heated wire, we may make two alternative hypotheses.

First Hypothesis.—Hydrogen exists on the surface in the form of atoms only. Molecules, formed by the combination of adjacent atoms, leave the surface immediately.

Second Hypothesis.—Hydrogen can exist on the surface in either molecular or atomic condition.

FIRST HYPOTHESIS

We assume that out of all hydrogen atoms striking a bare surface, the fraction α_1 condenses and that the corresponding fraction for the molecules is α_2.

Let ω be the velocity with which the dissociation of hydrogen is brought about by the heated wire. We shall express ω in gram molecules of hydrogen (H_2) dissociated per second per sq. cm. of surface.

The rate at which atomic hydrogen leaves the wire is $\nu_1\theta_1$. The rate at which it is taken up by the wire is $\alpha_1\theta\mu_1$. The net rate at which it is produced is the difference between these two, and this must be equal to 2ω.

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[9] In calculating μ in this case by (1) the value $M = 2$ will have to be used instead of $M = 1$.

The coefficient 2 is due to the fact that two atoms of hydrogen are produced from each molecule. We thus obtain the equation

$$2\omega = \nu_1\theta_1 - \alpha_1\theta\mu_1. \tag{4}$$

In a similar way we may consider the role played by the molecular hydrogen. Since we have assumed that molecular hydrogen does not exist as such on the surface, each molecule condensing on the surface must fill two adjacent elementary spaces as two separate atoms. The rate at which molecular hydrogen is removed by condensation on the heated wire is thus $\alpha_2\theta^2\mu_2$ gram molecules per sq. cm. per second. This process will be reversible. That is, adjacent hydrogen atoms on the surface may combine together to form molecular hydrogen which then escapes from the surface. The rate at which this occurs will evidently be $\nu_2\theta_1^2$, since the chance of two hydrogen atoms occupying adjacent positions will be proportional to θ_1^2. The coefficient ν_2 is the rate of evaporation when the surface is wholly covered by atomic hydrogen ($\theta_1 = 1$).

The difference between the two rates will be equal to ω, the rate at which molecular hydrogen disappears. Thus we obtain

$$\omega = \alpha_2\theta^2\mu_2 - \nu_2\theta_1^2. \tag{5}$$

The fractions θ and θ_1 must fulfill the condition[10]

$$\theta + \theta_1 = 1. \tag{6}$$

These three equations, 4, 5 and 6, enable us to calculate the equilibrium constant in the gas phase in terms of the quantities α_1, α_2, ν_1 and ν_2.

There are several possible definitions of the equilibrium constant, as follows:

$$K_p = p_1^2/p_2 \tag{7}$$

$$K_c = c_1^2/c_2 \tag{8}$$

$$K_\mu = \mu_1^2/\mu_2 \tag{9}$$

Here p_1 and p_2 are the partial pressure of atomic and molecular hydrogen in equilibrium with each other, while c_1 and c_2 are the corresponding concentrations. The third equilibrium constant K_μ as defined by (9) will be found very convenient in dealing with heterogeneous reactions. Since $p = c\mathrm{RT}$ the relation between K_p and K_c is

$$K_p = \mathrm{RT}K_c. \tag{10}$$

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[10] Provided the surface is perfectly clean. The presence of a gas (otherwise inert) which is strongly adsorbed on the surface will cause the larger portion of the surface to be covered with inert molecules (or atoms). Thus the Equation 6 becomes $\theta + \theta_1 = 1 - \theta_2$ where θ_2 represents the fraction of the surface covered by the inert substance. This theory of catalytic poisons will be developed in subsequent papers.

Similarly, from (2) we obtain, since $M_2 = 2$, and $M_1 = 1$

$$K_\mu = K_p/\sqrt{\pi RT} = K_c\sqrt{RT/\pi}. \tag{11}$$

In order to find the value of K_μ we place $\omega = 0$ which is evidently the condition for equilibrium. Equations 4 and 5 then reduce to

$$\mu_1 = \frac{\nu_1\theta_1}{\alpha_1\theta}, \tag{12}$$

$$\mu_2 = \frac{\nu_2\theta_1^2}{\alpha_2\theta^2}. \tag{13}$$

Whence by (9)

$$K_\mu = \left(\frac{\nu_1}{\alpha_1}\right)^2 \cdot \frac{\alpha_2}{\nu_2}. \tag{14}$$

It should be noted that θ and θ_1 cancel out in the derivation of this equation.

Since the factors α and ν are not functions of the pressure, Equation 14 expresses the law of mass action, which in this case follows automatically as a consequence of the mechanism we have assumed. From Equations 4 and 5 we can determine the values of the two factors in the second member of (14). Thus

$$\frac{\nu_1}{\alpha_1} = \frac{\frac{2\omega}{\alpha_1} + \theta\mu_1}{\theta_1} \tag{15}$$

$$\frac{\nu_2}{\alpha_2} = \frac{\theta^2\mu_2 - \frac{\omega}{\alpha_2}}{\theta_1^2}. \tag{16}$$

Substituting these in (14) gives

$$K_\mu = \frac{\left(\mu_1 + \frac{2\omega}{\alpha_1\theta}\right)^2}{\left(\mu_2 - \frac{\omega}{\alpha_2\theta^2}\right)}. \tag{17}$$

The value of θ may be found by solving (4) and (6) as simultaneous equations. We thus obtain

$$\theta = \frac{\nu_1 - 2\omega}{\nu_1 + \alpha_1\mu_1} = \frac{1 - 2\omega/\nu_1}{1 + \alpha_1\mu_1/\nu_1}. \tag{18}$$

The two Equations 17 and 18 give us a complete solution of our problem. They enable us to calculate the dissociation constant K_μ in terms of α_1, α_2, ν_1 and experimentally determined values of ω.

SECOND HYPOTHESIS

In this hypothesis we assume that hydrogen molecules striking the surface condense as such, each molecule occupying only one elementary space. The atoms which strike the surface condense as atoms. Interaction between the atoms and molecules on the surface occurs.

The rate of condensation of atomic hydrogen is $\alpha_1\theta\mu_1$ while the rate at which it evaporates from the surface is $\nu_1\theta_1$. Hence we have

$$2\omega = \nu_1\theta_1 - \alpha_1\theta\mu. \tag{19}$$

This is identical with Equation 4. The rate of condensation of molecular hydrogen is $\alpha_2\theta\mu_2$ whereas the rate of evaporation is $\nu_2\theta_2$. This gives

$$\omega = \alpha_2\theta\mu_2 - \nu_2\theta_2. \tag{20}$$

The rate at which hydrogen atoms combine will be proportional to the square of θ_1, since the chance that two atoms shall be in adjacent spaces is proportional to θ_1^2. We may thus place the rate of formation of molecular hydrogen from the atoms, equal to $\beta_1\theta_1^2$ where β_1 is the rate of formation when the surface is wholly covered with atomic hydrogen.

The rate at which hydrogen molecules dissociate into atoms on the surface will be proportional to the product of θ by θ_2 since a hydrogen molecule must be adjacent to a vacant space in order that it can dissociate. The chance that a hydrogen molecule and a vacant space shall be adjacent to each other is evidently proportional to $\theta\theta_2$. We may, therefore, place the rate of dissociation of hydrogen equal to $\beta_2\theta\theta_2$.

We thus obtain a third equation

$$\omega = \beta_2\theta\theta_2 - \beta_1\theta_1^2. \tag{21}$$

Finally we have the condition (in the absence of catalytic poisons)

$$\theta + \theta_1 + \theta_2 = 1. \tag{22}$$

If we substitute $\omega = 0$ in Equations 19, 20 and 21, we obtain the values of μ_1, μ_2, etc., corresponding to equilibrium conditions.

$$\mu_1 = \frac{\nu_1\theta_1}{\alpha_1\theta}, \tag{23}$$

$$\mu_2 = \frac{\nu_2\theta_2}{\alpha_2\theta}, \tag{24}$$

$$\frac{\beta_1}{\beta_2} = \frac{\theta\theta_2}{\theta_1^2}. \tag{25}$$

Substituting (23) and (24) in (9)

$$K_\mu = \left(\frac{\nu_1}{\alpha_1}\right)^2 \frac{\alpha_2\beta_2}{\nu_2\beta_1}. \tag{26}$$

From (19) we obtain

$$\frac{\nu_1}{\alpha_1} = \frac{\theta\mu_1 + 2\omega/\alpha_1}{\theta_1} \tag{27}$$

and from (20)

$$\frac{\nu_2}{\alpha_2} = \frac{\theta\mu_2 - \omega/\alpha_2}{\theta_2}, \tag{28}$$

while (21) and (25) give

$$\frac{\beta_1}{\beta_2} = \frac{\theta\theta_2}{\theta_1{}^2}\,(1 - \omega/\beta_2\theta\theta_2) \tag{29}$$

or

$$\frac{\beta_2}{\beta_1} = \frac{\theta_1{}^2}{\theta\theta_2}\,(1 + \omega/\beta_1\theta_1{}^2). \tag{30}$$

From (19) we obtain

$$\theta_1 = \frac{\alpha_1\theta}{\nu_1}\,(\mu_1 + 2\omega/\alpha_1\theta) \tag{31}$$

and from (20)

$$\theta_2 = \frac{\alpha_2\theta}{\nu_2}\,(\mu_2 - \omega/\alpha_2\theta). \tag{32}$$

By combining (26), (27), (28), (30) and (31), we obtain

$$K_\mu = \frac{\left(\mu_1 + \dfrac{2\omega}{\alpha_1\theta}\right)^2 + \left(\dfrac{\nu_1}{\alpha_1\theta}\right)^2 \cdot \dfrac{\omega}{\beta_1}}{\left(\mu_2 - \dfrac{\omega}{\alpha_2\theta}\right)}. \tag{33}$$

Similarly, from (26), (27), (28), (29) and (32)

$$K_\mu = \frac{\left(\mu_1 + \dfrac{2\omega}{\alpha_1\theta}\right)^2}{\left(\mu_2 - \dfrac{\omega}{\alpha_2\theta}\right) - \dfrac{\nu_2}{\alpha_2\theta^2} \cdot \dfrac{\omega}{\beta_2}} \tag{34}$$

The Equations 33 and 34 are different forms of the same fundamental equation.

By substituting (31) and (32) in (22), and solving for θ we find

$$\theta = \frac{1 + \frac{\omega}{\nu_2} - \frac{2\omega}{\nu_1}}{1 + \frac{\alpha_1\mu_1}{\nu_1} + \frac{\alpha_2\mu_2}{\nu_2}}. \tag{35}$$

These last three equations furnish a complete solution of our problem in the case of the second hypothesis.

COMPARISON WITH THE OLDER THEORY

It will be interesting to compare the results obtained by each of the above hypotheses, with those found by the theory developed in Part II of this paper. The Equations 21 and 26, of Part II (page 427), correspond to the Equations 17 and 33 derived above. However, since the nomenclature previously used differs from that employed here it will be worth while to go through the derivation of the older equation again by a method which will bring out clearly the difference between the two viewpoints.

It is assumed that out of all the atoms striking the surface, the fraction α_1 is *absorbed* by the metal, whereas for the molecules the corresponding fraction is α_2. It is assumed further that the surface of the metal contains hydrogen molecules and atoms in equilibrium with each other. Let v_1 and v_2 be the rates at which atomic and molecular hydrogen, respectively, escape from the surface.

We may thus derive the equations

$$2\omega = \nu_1 - \alpha_1\mu_1 \tag{36}$$

$$\omega = \alpha_2\mu_2 - \nu_2, \tag{37}$$

from which we obtain

$$\nu_1 = 2\omega + \alpha_1\mu_1 \tag{38}$$

$$\nu_2 = \alpha_2\mu_2 - \omega. \tag{39}$$

It is assumed that the equilibrium inside the metal obeys the law of mass action, so that the concentration of molecular hydrogen is proportional to the square of the concentration of atomic hydrogen. It is further assumed that the rates at which each of the gases escapes from the surface, is proportional to the corresponding concentration in the metal. Thus, v_1^2/v_2 is a constant proportional to the equilibrium constant in the metal. Let this constant be represented by A. Then we have by (38) and (39)

$$A = \frac{(\alpha_1\mu_1 + 2\omega)^2}{(\alpha_2\mu_2 - \omega)}. \tag{40}$$

When equilibrium exists in the gas phase, we may place $\omega = 0$ and thus find

$$A = \frac{\alpha_1{}^2\mu_1{}^2}{\alpha_2\mu_2} = \frac{\alpha_1{}^2}{\alpha_2} K_\mu. \qquad (41)$$

Combining (41) and (40) gives

$$K_\mu = \frac{\left(\mu_1 + \frac{2\omega}{\alpha_1}\right)^2}{\left(\mu_2 - \frac{\omega}{\alpha_2}\right)}. \qquad (42)$$

This is the equation which was derived in Part II and which was found to be in excellent agreement with the results of the experiments. In fact, we may look upon this equation as having been proved correct by the experiments.

When we compare this equation with (17), which was calculated by the 1st hypothesis, we see that the two become identical if we place $\theta = 1$. We see by (18) that this condition will be fulfilled if ν_1 is very large, compared to $\alpha_1\mu_1$ and ω. We may thus conclude that the first hypothesis is entirely in agreement with the experiments if we assume that ν_1, the rate of evaporation of hydrogen from the surface, is so high that only a small fraction of the surface remains covered.

If we compare Equation 42 with 33 and 34, we see that they become identical if we take $\theta = 1$ while β_1 and β_2 are taken to be very large. This last requirement means the velocity with which adjacent hydrogen atoms or molecules interact or dissociate must be very large compared to that at which they evaporate. This is equivalent to assuming that equilibrium exists between the atoms and molecules on the surface. Thus we see that the second hypothesis is also in accord with the experiments if the rate of evaporation is assumed to be so high that only a small fraction of the surface is covered.

The experiments thus do not enable us to decide between the two hypotheses. In fact, it is also possible by means of slightly different hypotheses from those described here to obtain the same equation.

But all these hypotheses have this in common: they lead to the conclusion that only a small fraction of the surface is covered with hydrogen atoms or molecules, and that the reaction is not dependent upon phenomena occurring within the surface of the metal.

This conclusion that only a small fraction of the surface is covered with hydrogen is confirmed by other facts.

We have seen that the accommodation coefficient of hydrogen in contact with tungsten at relatively low temperatures is about 19%, whereas at high temperatures 68% of the molecules which strike the filament reach chemical equilibrium. The explanation of this apparent paradox, according to the new theory, is that the surface of the tungsten is largely covered by adsorbed hydrogen at the lower temperatures, whereas at the higher temperatures it is practically bare. The 19% thus corresponds to the fraction of molecules which condenses when they strike a surface already covered with hydrogen, while the 68% represents the fraction condensing on a bare surface.

Another fact which proves nearly conclusively that the surface of a highly heated tungsten wire is not covered to an appreciable extent by hydrogen is that the electron emission from tungsten is not perceptibly influenced by the presence of pure hydrogen.[11] A large amount of unpublished work in this laboratory has demonstrated that the electron emission affords an extraordinarily sensitive method of detecting the presence of a film of adsorbed material, so thin that it only partly covers the surface with a layer one atom deep. Some of this evidence will soon be published.

In subsequent papers, the theory of heterogeneous reactions here outlined, will be applied to a large number of reactions. It will be shown that the equations derived by Fink, in his work on the contact sulfuric acid process, may also be derived by the new theory, and that definite proof that the mechanism postulated by Bodenstein and Fink cannot apply in this work may be adduced from the experiments themselves.

The work of Bodenstein and Ohlmer on the reaction between carbon monoxide and oxygen is also in quantitative agreement with the new theory. Other cases, including several studied experimentally in this laboratory, will also be discussed.

SUMMARY

1. The velocity of the reaction by which hydrogen is dissociated in contact with a heated tungsten wire is so enormous that it definitely proves that the reaction cannot depend upon a diffusion of hydrogen into the metal even if the depth of penetration should be only that of a single atom.

2. A general theory of heterogeneous chemical reactions is outlined in which the reaction is assumed to take place in the actual surface layer of atoms.

3. This theory is worked through in detail for the case of the dissociation of hydrogen. It leads to equations which become identical with that previously derived by other methods, when it is assumed the hydrogen

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[11] Langmuir, *Phys. Z.*, *15*, 523 (1914).

evaporates so rapidly from the surface that only a negligible fraction of the surface is covered at any time. This equation has already been shown to be in full agreement with the experiments (Parts I and II).

4. The conclusion that very little of the surface is covered is in good accord with the fact that the accommodation coefficient of hydrogen is 0.19 at temperatures below 1500° K., while the "chemical" accommodation coefficient α_2 for the dissociation of hydrogen is 0.68 at high temperatures.

5. The fact that the electron emission from heated tungsten is not affected by the presence of pure hydrogen is additional evidence that the fraction of the surface covered by hydrogen atoms or molecules must be very small.

Chapter Ten

FORCES NEAR THE SURFACES OF MOLECULES

In the early development of the kinetic theory, during the last century, it was usual to consider the molecules of gases as rigid spheres, which exerted no forces on one another except at the instant of contact. In this way it was possible to account quantitatively with fair accuracy not only for the effects of pressure and temperature on the volume, but also for the viscosity, heat conductivity, and diffusion of gases, and other phenomena involving the free paths of the molecules.

By considering also attractive forces which varied with some power of the distance between the centers of the molecules, van der Waals was able to account for the main features of the transition from the gaseous to the liquid state, and also explained in a satisfactory manner the departures from the ideal gas laws which are shown by all gases at high pressures.

As new properties of matter are brought into consideration, or as a deeper understanding of them is needed, it is necessary to postulate additional properties of the molecules, and to know more accurately the nature of the forces acting between them. For example, to deal with the properties of electrolytes it is necessary to consider electric charges on the molecules or ions. In 1912 Debye showed that the electrical properties of many dielectrics could be accounted for by assuming that the center of gravity of the electrons in a molecule did not coincide with the center of gravity of the positive charges of the nuclei. Thus the molecule possessed what we call a dipole moment, which can be measured as the product of an electric charge by the distance through which it is displaced. It is found, for example, that a molecule of water possesses a dipole moment of 1.8×10^{-18} electrostatic units. A moment of this magnitude could be produced by having an electron at a distance of 0.37×10^{-8} cm. from a proton. Since there are 10 electrons in a water molecule, it is only necessary that the center of gravity of these electrons shall lie at a distance of 0.037×10^{-8} cm. from the center of gravity of the three nuclei in the molecule. Thus displacements of the electrons to distances minute compared with the diameter of the molecule can account for even the largest values of dipole moments that have been observed.

H. B. Hardy (1) in 1912 and the writer (2) (3) in 1916 pointed out that the fields of force around many chemical molecules must be very unsymmetrical, and that this resulted in an orientation of the molecules at the surfaces of liquids and in adsorbed films on solids. It was also found that the shapes which the molecules could assume, and which were determined by their chemical structures, were of great importance in connection with such properties as surface tension.

Within recent years, particularly through the work of Debye and his students, a great deal of knowledge has been accumulated regarding the electrical forces in liquids and solutions which contain ions and dipoles Particularly in the study of electrolytes has this work cleared up many of the most serious difficulties of earlier theories.

There is now no need of drawing distinctions between chemical and physical forces. The chemist recognizes that many of the forces with which he has been dealing are electrical in nature, for, after all, molecules are built up of electrons and positive nuclei, and their interactions must necessarily be electrical. However, the simple classical theory of electrical forces based on Coulomb's law is wholly insufficient to account for chemical properties. With charged particles obeying Coulomb's law only, the minimum of potential energy is obtained when the positive and negative particles coincide. There must be something corresponding to repulsive forces holding the particles apart.

REPULSIVE FORCES BETWEEN MOLECULES

In many of the later developments of the kinetic theory where the molecules were regarded as rigid spheres, the repulsive forces which must counteract the attractive forces were assumed to act only during collisions—that is, at the instant of contact of the spheres (4). No explanation was attempted of the internal forces within the molecule which could result in this repulsion between molecules.

In order to account for the compressibility of solids, Born and Landé (5) have assumed that the repulsive force between molecules (or ions) varies inversely as a power of the distance between the centers of the molecules. Thus in the case of halide salts of the alkalies, such as NaCl, KI, etc., they showed that the compressibility indicated that the repulsive force varied inversely as the tenth power of the distance, while the attractive force resulting from the charges on the ions varied inversely as the square, in accord with Coulomb's law. Born (6) also attempted to show that the inverse tenth power law for repulsion could be deduced by assuming that the electrons and the ions were arranged with cubic symmetry as at the corners of a cube. This attempt, however, must be regarded as a failure for two reasons. First, the method of mathematical expansion which was used is not legitimate when applied to distances as short as those between ions in salts; and, second, Born assumed that the cubical ions were all orientated so that their edges were parallel. This kind of orientation would be unstable under the forces assumed, for these forces would tend to orientate one cubical ion so that its corner would come opposite the face of another ion, and in this case the repulsive force would be replaced by an attractive force which would act in addition to the force between the ionic charges. Although such orientation of ions as Born assumes might conceivably exist in solid crystals from causes which he does not discuss, it is clear that it cannot be the cause of the repulsive forces, since the elimination of the orientation by melting the salt does not greatly alter the density or the compressibility.

Debye (7) has developed a theory which seems to give a better picture of the repulsive forces. Assuming the electrons to move in orbits in accord with Bohr's theory, he finds that the electric field around a molecule is a pulsating or partly oscillating field increasing in amplitude very rapidly as the surface of the molecule is approached. Thus when an electron approaches a molecule it acquires, in addition to any motion of translation it may have, an oscillatory motion due to the pulsating field. Debye shows that this oscillatory motion tends to be 180° out of phase with the field producing it, and then shows, that because of the non-uniformity of the electric field near an atom the resulting force will be one of repulsion.

On this theory the repulsive forces between molecules are due to the perturbations in the electron orbits in one molecule, caused by the motions of the electrons in their orbits in the neighboring molecules. The repulsive force thus does not originate from a molecule as a whole, but comes from the close approach of electrons in the two molecules. This would seem to indicate that we may profitably regard these forces as *surface forces,* and should express them as functions of the distances between the surfaces of the molecules rather than in terms of the distances between the centers. This conception affords a justification, to a large extent, of the theory which regarded molecules as rigid elastic spheres.

Even if we accept Debye's picture of the origin of repulsive forces, we see that it really only refers the cause back to the quantum theory, by which the stable orbits of the electrons in the molecule are determined. At present, however, problems of this kind are treated by wave mechanics instead of by a consideration of orbits of electrons. For a few simple cases, such as interactions between hydrogen molecules, Hund and London have been able to calculate the forces by means of wave mechanics. But it will probably be a long time before definite knowledge of repulsive forces can be obtained in this way for more complicated molecules.

The quantum theory teaches that each electron in an atom is characterized by four quantum numbers, which are integers. Not all quantum numbers are possible; there are, for example, certain conditions (selection rules) which they must satisfy. The normal atom or molecule, with which the chemist is concerned, is one in which the electrons are so arranged that the total energy is a minimum, subject to the quantum rules that must be fulfilled.

It seems that the factor of greatest importance to the chemist is that which is known as the Pauli principle, which states that no two electrons in an atom can have the same combination of four quantum numbers. It is this principle which underlies the Periodic Table of the elements, and in a similar manner determines the arrangement of electrons in a molecule. It is through the development of methods of this kind that our greatest hope lies in obtaining a better understanding of the nature of repulsive forces.

For most practical purposes it is best for the chemist to regard molecules of organic substances as having shapes suggested by chemical structural formulas, and as having surfaces which are rather rigid so that strong repulsive forces are called into play for only moderate deformations. For many purposes it is still useful to look upon the surfaces as completely rigid.

ATTRACTIVE FORCES BETWEEN MOLECULES[1]

Whereas the quantum theory seems essential in an understanding of the repulsive forces, the classical laws, such as the Coulomb law, are largely sufficient for dealing with the attractive forces between molecules. For example, the Debye-Hückel theory of electrolytes (8) is based on the Coulomb law, the Poisson equation, and the Boltzmann equation—all laws of classical mechanics.

In discussing forces between molecules, Debye has classified molecules in three groups: "(1) ionic, (2) polar and (3) non-polar." The ionic type is represented by electrolytic ions, such as K^+, NO_3^-, etc., and gaseous ions. In these molecules the number of electrons is unequal to the number of positive charges of the nuclei of atoms, so that the molecule as a whole has an electric charge which is some multiple of e, the charge of an electron. The polar type is represented by molecules which have a dipole moment—that is, uncharged molecules in which the center of gravity of the negative charges does not coincide with that of the positive. Non-polar molecules thus include all molecules which are uncharged and in which the centers of gravity of the positive and negative particles coincide. From Debye's point of view such molecules may correspond to quadrupoles, octopoles, etc. For example, positive and negative charges arranged alternatively at the corners of a square will give a quadrupole, at the corners of a cube an octopole. In forming clear conceptions of the attractive forces between molecules it is useful to consider the actual magnitude of the forces involved.

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[1] The term "molecule" is to be used in its broad sense, which includes atoms and ions.

IONS

The electric field at a distance r from a univalent ion having a charge e is $e/\varepsilon r^2$, where ε is the dielectric constant of the medium. The charge of the electron, e, is equivalent to 1.43×10^{-7} volt centimeter and thus the electric field is $1.43 \times 10^{-7}/\varepsilon r^2$ volts per centimeter, and the electric potential corresponding to this force is $1.43 \times 10^{-7}/\varepsilon r$. If we take for r the value 3×10^{-8} cm., which corresponds roughly to the distance between two ions in contact, we find the electric field to be 1.6×10^8 volts per centimeter and the potential to be 4.8 volts. Taking for ε the value 80, corresponding to the dielectric constant of water, we would obtain values only one-eightieth of those given. However, it is doubtful if the conception of dielectric constant is entirely justified at distances as short as this for we can hardly speak of two molecules in contact as being in a medium having known electrical properties. At distances several times greater than the molecular diameter the use of dielectric constant in this way is justified.

The applications of the Debye-Hückel theory to electrolytes prove that the forces at these larger distances are of vital importance in an understanding of the properties of ions. According to the Coulomb law the force between two ions varies inversely as the square of the distance. In electrolytic solutions the increased concentration of positive ions around negative ions, and vice versa, causes the force between two given ions to decrease with increasing distance more rapidly than according to the inverse square law.

POLAR MOLECULES

At a distance r from a dipole molecule having an electric moment μ the electric potential is $\mu \cos \theta/r^2$, where θ is the angle between the radius vector r and the axis of the dipole. It can thus be found that at a distance r along the dipole axis the electric field is $-2\mu/r^3$, this force being in a direction of the polar axis. At a distance r in the equatorial plane of the dipole the electric force is also in a direction parallel to the polar axis but has the magnitude $+\mu/r^3$.

Debye (9) has shown that in general because of thermal agitation a dipole (or quadrupole) molecule in a gas or liquid is changing its orientation so fast that we must not regard the force produced by a dipole as a steady force, but a rapidly fluctuating force, and under these conditions many of the effects produced by the force are proportional to $\overline{E}^2$ or the mean square field. The effective force can thus vary inversely as the sixth power of the distance from the dipole.

NON-POLAR MOLECULES

If the molecule is a quadrupole the instantaneous force in any given direction will vary inversely as the fourth power of the distance, and thus the effective fluctuating force will vary inversely as the eighth power of the distance. With more symmetrical molecules the forces will vary inversely with still higher powers of the distance.

Under the influence of forces of the kinds we have been considering the various types of molecules in liquids respond in different ways. Positive ions tend to concentrate around negative ions in the manner considered by the Debye-Hückel theory (8). Dipole molecules tend to be orientated by the field in the neighborhood of the ion. Thermal agitation tends to prevent this orientation, so that only when the dipole molecule is very close to the ion is the orientation of the molecule complete.

The dipole molecule, orientated in a field, tends to move in the direction towards which the field is of greater intensity. The change in potential energy is mE, where E represents the change in field strength and m is the effective dipole moment (average moment) in the direction of the field.

A field insufficient to orientate the dipoles completely gives an effective dipole moment m, which according to Debye (10) is

$$m = \mu^2 F/3kT$$

where F is the electric force tending to produce the orientation. Since the energy available for producing motion of translation in a dipole is proportional to mF, we see that at large distances dipoles attract one another in proportion to F^2 and therefore in inverse proportion to the sixth power of the distance. If, however, we consider a fixed dipole (for example one attached to a large organic molecule) acting on another dipole at a very short distance so that the latter is orientated by the field of the former, then the force of attraction will vary inversely as the fourth power of the distance.

An electric field of intensity F, acting on a non-polar molecule, causes a deformation, or polarization, of the molecule so that it acquires a dipole moment m given by

$$m = \alpha F$$

where α is the polarizability. A liquid made up of non-polar molecules of this kind will have a dielectric constant ε which is greater than unity, and the *molar polarization* of the liquid is calculated from ε by means of the equation

$$P = \left(\frac{\varepsilon - 1}{\varepsilon + 2}\right)\frac{M}{\rho}$$

where M is the molecular weight and ρ is the density of the liquid. The relation between P and α is given by the equation

$$P = \frac{4\pi}{3} N\alpha = 2.54 \times 10^{24}\,\alpha$$

where N is the Avogadro number, 6.06×10^{23}. The quantity P has the dimensions of a volume and is thus measured in cubic centimeters. For ordinary organic liquids the value of P is roughly about 0.3 of the volume of a gram-molecule. A few values of P and α are given in table 1. From the value $\alpha = 10^{-23}$, which is of the order of magnitude found in most organic liquids, we can calculate that the electric field needed to give to a non-polar molecule a dipole moment of 10^{-18} is $F = 3.0 \times 10^{7}$ volts per centimeter. This is the field that would exist at a distance $r = 7 \times 10^{-8}/\sqrt{\varepsilon}$ cm. from an electron. A field of this magnitude would be found at the distance $r = 2.7 \times 10^{-8}/(\varepsilon)^{1/3}$ in the direction along the axis of the dipole.

From the foregoing discussion, we see that the effects of the electric fields of molecules are of three kinds which we may classify as (1) segregation, (2) orientation, and (3) deformation. As an example of segregation, we have the segregation of positive ions around negative ions in electrolytes. Dipole molecules become orientated in the field produced by any other molecule and thus are attracted toward the molecule producing the field. Non-polar molecules, under the influence of fields of other molecules, become deformed or polarized so that they acquire a dipole moment in the direction of the field and are thus attracted by the molecule producing the field.

TABLE I

VALUES OF P AND α

	P	α
	cc.	
H_2	5.8	2.28×10^{-24}
N_2	13.6	5.4
CH_4	21.0	8.3
C_6H_6	25.8	10.2

In estimating quantitatively the magnitude of the segregation and orientation that result from molecular fields, we may apply the Boltzmann equation;

$$\frac{n_1}{n_2} = A\varepsilon^{\lambda/kT}$$

where n_1 and n_2 represent the relative numbers of molecules in two given positions, or orientations, and λ is the work done in transferring a molecule from one of these states to another. The constant A involves the ratio of the *a priori* probabilities of the molecules in the two regions or states under consideration. These probabilities are frequently dependent upon geometrical factors, but often involve a knowledge of the quantum phenomena accompanying the change in state. The quantity ε in this equation is the base of the natural system of logarithms, 2.718; k is the Boltzmann constant, 1.37×10^{-16} erg per degree; T is the absolute temperature.

We see from the Boltzmann equation, that when the constant A is not too far removed from unity, the effects of segregation and orientation usually begin to be important only when the energy λ becomes of the same order of magnitude as kT. At room temperature the value of kT is 4.1×10^{-14} erg, which is the energy that an electron would acquire in falling through a potential of 0.025 volt.

In Debye's theory for the contribution of dipole molecules to the dielectric constant of liquids, it is shown that the effective dipole moment m of the dipole molecules (of moment μ) is $\frac{1}{2}\mu$ when the field is of such intensity that the work done by the field in orientating the molecule is equal to $2kT$.

The segregation of ions of one sign around an ion of the opposite sign will be marked at distances r less than that at which the potential is 0.025 volt; that is when r is less than $57 \times 10^{-8}/\varepsilon$ cm. If ε has a low value, of a few units only, then even in very dilute solutions, where the distances between the ions are more than ten times greater than the molecular diameters, the ions will tend to be swept out of the solution and brought into contact with each other. This is in accord with the fact that such salt-like substances as NaCl, whose crystals are held together by forces of the Coulomb type, are practically insoluble in organic liquids of low dielectric constant. On the other hand, in water and other liquids of high dielectric constant, in solutions of even moderate concentration, the ions are far enough apart so that their potentials with respect to one another are less than kT, which agrees with the fact that these salts are soluble in these liquids, and that their solutions behave as electrolytes.

We have seen that to orientate the larger portion of dipole molecules in liquids requires a field F which makes μF greater than $2\ kT$. This means that a field of about 2.4×10^7 volts per centimeter is needed for the orientation. The work done when the orientated molecule is brought into the field is of the same order of magnitude, so that a field sufficient to cause nearly complete orientation of dipole molecules will also cause marked segregation. A field of 2.4×10^7 will exist at a distance $r = 8 \times 10^{-8}/(\varepsilon)^{1/2}$ cm. from a univalent ion, or at a distance $r = 3 \times 10^{-8}/(\varepsilon)^{1/3}$ cm. along the axis of a dipole molecule having a moment $\mu = 10^{-18}$. In other directions than along the dipole axis the force will be less and therefore the distance at which effective orientation or segregation occurs will be less than that just given.

From these calculations we conclude that the interaction between dipole molecules of moment 10^{-18} can cause mutual orientation only when they are practically in contact. If they were separated by one additional molecule, so that the distance between centers is 6×10^{-8} cm., even if they were still orientated, the force would be only one-sixteenth as great, since it varies inversely as the fourth power of the distance. However, at this greater distance, the orientation would be far from complete, so that the force would actually vary inversely as the sixth power of r, and would thus be only one sixty-fourth as great as if the molecules were in contact.

The electric force necessary to deform a molecule sufficiently to give it a dipole moment $\mu = 10^{-18}$ (viz., 3×10^7 volts per centimeter) is practically the same as that needed to produce orientation of a dipole molecule having this same moment. Thus when two dipole moment molecules are in contact, the dipole moment which each possesses is practically doubled because of their mutual deformation.

Taking the electric field near a dipole to be proportional to r^{-3}, and remembering that the distance between the center of one molecule and the surface of its neighbor is only one-third the distance to the surface of the far neighbor, we realize that the electric field intensity at one side of the dipole molecule is twenty-seven times as great as at the opposite side.

The latent heat of evaporation of a liquid expressed per molecule gives the energy which must be expended to separate the molecules of liquid from one another. Pentane, a non-polar liquid, which boils in the neighborhood of room temperature (36°C.), has a heat of evaporation of about 40×10^{-14} erg per molecule, which is roughly equal to $10\ kT$. According to the rough empirical rule of Trouton, the absolute boiling points of liquids are proportional to their latent heats of evaporation, so that in general, to the same degree of approximation, the heats of evaporation per molecule for all liquids will be about $10\ kT$, where T is the temperature at the boiling point. This can be looked upon as a consequence of the Boltzmann law. The coefficient A in this case, however, is quite different from unity.

The energy involved in the close approach of ions to within molecular dimensions is far greater than 10 kT—at least when the medium is one of low dielectric constant. Thus we are not surprised at the fact that substances built up of ions are solid bodies which melt and boil only at very high temperatures, and are soluble only in liquids of high dielectric constant.

We have found that the energies involved in the approach of dipole and non-polar molecules (having values for μ of about 10^{-18}, and for α of 10^{-23}) to within a distance of 3×10^{-8} cm. is approximately equal to kT ($T =$ 300°K). Since a given molecule will usually be in contact with about a dozen others, it is to be expected that the energy necessary to separate a molecule from all its neighbors would be of the order of magnitude of 10 kT. In fact, we can reasonably expect values larger than this because of the fact that the greatest effects will be produced in the deformation of the molecule on its side facing the adjacent molecule ($r = \frac{1}{2}$ molecular diameter), the electric field there being about eight times greater than at the center of the molecule.

We thus have an explanation of the fact that liquids whose molecules have the properties we have postulated will, in general, have boiling points considerably above room temperature. When the molecules are in contact the energies of the non-polar molecules are not very greatly different from those of the dipole molecules—at least are of the same order of magnitude. In this we have an explanation of the fact that the boiling points of liquids containing dipole molecules are only moderately higher than those of non-polar substances. It is possible, for example, to have liquids whose molecules are dipoles, such as anhydrous hydrogen chloride, which boil at temperatures far below room temperature.

Our analysis of the known electrical forces causing the interactions of molecules thus leads us inevitably to the conclusion that the forces involved in holding together the molecules of organic liquids are acting almost wholly between molecules *in contact,* and that in general no serious error would be made in neglecting all forces which act at greater distances. This conclusion is, I believe, thoroughly justified in the case of all liquids built up of non-polar molecules. It applies with reasonable accuracy to most liquids having molecules containing dipoles. But in general, where liquids contain free ions the range of the forces is much greater, and we must then take into account the Coulomb forces which act at greater distances.

For many years, in connection with studies of adsorption, surface tension, and the kinetics of heterogeneous reactions, the writer has found it extremely useful to explain these phenomena in terms of actions between molecules *in contact.* From an empirical point of view the results have justified this method of attack. In many ways this conception is in accord with chemical tradition, for the chemist has always considered that chemical action between molecules takes place between molecules in contact.

The physicist, probably ever since the time of Newton, has been rather inclined to consider forces which vary as some power of the distance, or to deal with fields of force which extend throughout space. The remarkable success of the physicist in the development of the atomic theory, and more recently, in some of the applications to chemical phenomena, such as those involved in the properties of electrolytes, seems to have made many chemists and physicists believe that these methods would also provide the solutions to more complicated chemical problems.

It must be emphasized, however, that the physicist, in attempting to calculate the manner in which dipole molecules or non-polar molecules will interact in liquids, meets problems which are mathematically so complicated that it is necessary to make simplifying assumptions. For example, the potential energy of dipole or non-polar molecules with respect to one another is expressed as an infinite series in which the successive terms involve as factors $1/r$, $1/r^2$, $1/r^3$, etc. The coefficient of the first term for the case of dipole molecules is 0, the coefficient of the second term is then calculated with great care and often with great difficulty; and although the coefficients of the third and subsequent terms are known not to be zero, these terms are neglected because of the fact that they involve higher powers of r. We have seen, however, that the forces which are primarily important in liquids are those between molecules in contact, and that a small increase in the distance causes the forces to become very small. For example, with a force varying with $1/r^9$, such as Debye finds with non-polar molecules, the energy involved in the approach of two molecules would fall to one-half value if the distance between the molecules were increased 15 per cent. This change in energy has its effect in the exponent of the Boltzmann equation, so that most of the actions of importance must occur with only still smaller variations in the distance r. It is obvious, therefore, that even for the roughest kind of approximation one is not justified in neglecting the term involving $1/r^3$ in comparison with that which involves $1/r^2$.

As another example of the kinds of approximation that are necessary in treating mathematically the forces between dipole molecules, we have Debye's treatment of the relations between dielectric constant and chemical association (11). He considers the effect of dipoles on one another as the concentration of the dipolar molecule increases in a non-polar solvent. Assuming the molecules to be spheres, complicated equations are derived allowing for the interactions. The result is that the dipole moment per molecule increases with concentration because the molecules tend to line up along a common axis. This is due to the fact that the force along the polar axis is twice as great as in the equatorial plane for a given value of r. An analysis of experimental data, however, shows that in solutions of many dipole substances in non-polar solvents, the polarization per molecule decreases as the concentration increases. Such a result could be explained if the molecule instead of being a sphere were ellipsoidal with the equatorial diameter less than 80 per cent of the polar diameter. The introduction of such a concept would introduce far too great mathematical complications to make an analysis worth while.

Perhaps the greatest objection to a mathematical treatment of the properties of liquids in terms of power laws of force is that it becomes practically impossible to take into account the effects resulting from the complicated shapes of molecules which must characterize organic substances, according to the structural formulas of the chemist. If now we assume that the forces between molecules come into play only at their areas of contact, we have simplified the problem mathematically to such an extent that we can take into account our knowledge regarding the shapes of the molecules which can be furnished us by the chemist. Of course, in so doing we are making approximations, but the errors so introduced will, I believe, usually be far less than those which are often made by the physicist in dealing with these problems. I should like to outline now the ways in which a conception of surface forces can be developed to give concrete pictures and quantitative results for many problems which are too difficult to handle by the method involving the power laws of force.

In considering that the interactions between molecules occur at their surfaces of contact, it is not necessary to assume that the nature of the forces at any given part of the surface is characteristic wholly of the atom underlying the surface. The chemist knows, for example, that the properties of an organic molecule are not simply the sum of the effects due to the separate atoms in the molecule. If one of the hydrogen atoms in the methyl group of acetic acid be replaced by a chlorine atom, the effect of the greater charge on the kernel of the chlorine atom as compared with that of the hydrogen atom which it replaces, is to displace the electrons in the carboxyl group in the direction towards the chlorine atom. This displacement of the pair of electrons which hold the nucleus of the hydrogen atom of the carboxyl group causes the hydrogen nucleus to be held less firmly, and thus makes it easier for the hydrogen nucleus to pass over to a water molecule (in aqueous solutions of acetic acid) to form an OH_3^+ ion, which is the so-called hydrogen ion characteristic of acids. We thus have a clear indication of an alteration in surface forces which may extend over the whole surface of the molecule as a result of the replacement of a hydrogen atom by a chlorine atom.

We may form a clearer conception as to the magnitude of these changes in the surface forces due to effects transmitted from atom to atom in the molecule, by considering the chlorine-substituted fatty acids. In table 2 the values of the dissociation constant K for some of these acids are given as taken from Landolt-Börnstein tables. In the third column, under the heading ln r, is given the natural logarithm of the ratio of K for the acid in question to the value of K for normal acetic acid. According to the Boltzmann equation, this quantity should be equal to λ/kT, where λ represents the difference between the work necessary to remove a hydrogen ion from the given acid molecule and from an acetic acid molecule. Since kT is equivalent to 0.025 volt, we can obtain the value of λ in volts by multiplying the values of ln r by 0.025; the last column of the table gives these values.

TABLE II

Dissociation Constants of Chlorine-substituted Fatty Acids

	K	$\ln r$	VOLTS
Acetic acid	1.85×10^{-5}	[0]	0
Chloroacetic	155.0	+ 4.44	0.1053
Dichloroacetic	5000.0	7.6	0.190
Trichloroacetic	20000.0	9.3	0.233
Propionic acid	1.4×10^{-5}	[− 0.26]	− 0.006
α-Chloropropionic	147.0	4.36	0.1045
β-Chloropropionic	8.6	1.53	0.0382
Butyric acid	1.5×10^{-5}	[0.21]	− 0.0053
α-Chlorobutyric	139.0	4.30	0.1038
β-Chlorobutyric	8.9	1.57	0.0392
γ Chlorobutyric	3.0	0.48	0.012

Comparing the monochloro acids with each other, we see that all three of the acids in which the chlorine is in the α-position give $\lambda = 0.105$ volt. The two acids with chlorine in the β-position give $\lambda = 0.039$ volt. The single γ-chloro acid for which data are available gives $\lambda = 0.012$ volt.

From theoretical considerations we should expect that any state of strain which is transmitted from atom to atom along a hydrocarbon chain should decrease exponentially as the distance increases. The above data thus leads to the conclusion that the electric polarization produced by the presence of a chlorine atom in a hydrocarbon chain decreases in the ratio 2.7 : 1 in being transmitted from one carbon atom to the next. If instead of chlorine we should substitute other radicals, we might obtain electric forces of different magnitudes, but in any case we should expect this ratio 2.7 : 1 to apply to the decrease in the force from atom to atom. A considerable effect is thus transmitted from one atom to the next, but very little is transmitted as far as the second or third atom.

This result justifies us in attributing definite properties to different parts of the surface of the molecules of aliphatic compounds. For example, the field of force around a carboxyl group in a fatty acid should be independent of the length of the hydrocarbon chain, provided that this is more than about two carbon atoms long. That is, the forces near the surface of the carboxyl group should be practically constant for all the acids higher than propionic acid and would be roughly the same in the case of acetic acid, but might be considerably different in the case of formic acid. Similarly, we should not be able with any reasonable accuracy to regard the field of force around the carboxyl group as due merely to the super-position of the effects of the hydroxyl group and the carbonyl group, for these two groups are too close together in the molecule to be without important effect on one another.

PRINCIPLE OF INDEPENDENT SURFACE ACTION

From the foregoing analysis of the forces acting between molecules of various types, we conclude that there is a large class of substances for which we are justified in regarding the forces between two molecules in contact as being dependent mainly on the nature of the surfaces of the molecules which are in contact. This principle of independent surface action (12) will always be only an approximation to the truth, but there are many cases where it applies with sufficient accuracy and so greatly simplifies the problems of the interactions between molecules that useful results are obtained in problems so complex that no solution is otherwise possible. Let us consider some of these problems.

The theory of adsorption in monomolecular films on solids and liquids (13) is an example of the application of this principle. According to this theory, the force which holds an adsorbed molecule or atom on a surface depends on the character of the surface of contact between the molecule and the solid. If a second layer of molecules should form, the forces holding the molecule to the second layer are thus entirely different from those holding the molecules of the first layer. The rates of evaporation of the molecules from the first layer or from the second layer will differ greatly, especially since they depend upon the magnitude of the forces according to an exponential relation of the Boltzmann type. Two general cases must be considered. If the forces holding the molecules in the first layer are greater than those holding those of the second, there will be a wide range of pressures of the adsorbed gas for which the film will never exceed one molecule in thickness. We thus arrive at the conception that a certain fraction, θ, of the surface is covered by adsorbed molecules, and that the properties of this adsorbed film depend primarily on θ. If the forces between these molecules and the underlying surface are very large compared to those that act between adjacent molecules, then, for example, we may conclude that the rate of evaporation of the adsorbed molecules will be proportional to θ. This simple conception leads to an adsorption isotherm which has been found to hold experimentally in a large number of cases. However, if the forces that act between adjacent adsorbed molecules are not negligible, there will be large deviations from this simple law, but the theory may be easily extended to take into account such forces. The forces may be those of attraction, or, if the molecules become dipoles as a result of the adsorption, or if they become crowded, their interaction may cause repulsive forces.

The second important case (14) to be considered is that in which the forces that hold the second layer of molecules are greater than those which hold the first; or, more generally, the case in which the forces acting between adjacent adsorbed molecules are greater than those with which each of these is held on the underlying surface. There is then great difficulty in getting any appreciable number of molecules in the first adsorbed layer, and single molecules or atoms or groups of molecules in the first layer act as nuclei from which large aggregates or crystals may develop. The condensation of cadmium or mercury vapor on cooled glass surfaces is an example of this type. It is possible to formulate the problem quantitatively and to express the number of nuclei that will form per second as a function of temperature and pressure. The calculated values are in good agreement with those obtained by experiment. If definite numbers of isolated copper atoms are evaporated on to a clean surface, each one serves as a nucleus for the formation of cadmium crystals, when the temperature of the surface and the pressure of the cadmium vapor are carefully regulated, and thus by dark field illumination of the surface the copper atoms can be directly counted. Some experiments made several years ago by Mr. Harold Mott-Smith have shown that this method can be developed to count atoms just as the C. T. R. Wilson method can be used to count ions.

In case the adsorbed atoms on a metallic surface are electrically charged or acquire large dipole moments, electrical forces are brought into play which may make the principle of independent action inapplicable. For example, the rate of evaporation of electrons from a tungsten surface at high temperature is enormously increased by the presence of adsorbed thorium (15) or caesium (16) atoms on the surface. But the increase in the number of electrons which evaporate is not even approximately proportional to the amount of thorium or caesium which is present on the surface. The same is true for the evaporation of positive caesium ions from a tungsten surface. In both of these cases, the heat of evaporation of electrons or ions varies approximately linearly with θ, the fraction of the surface covered by the adsorbed atoms, and thus, according to the Boltzmann equation, the logarithm of the rate of evaporation of electrons or ions varies linearly with θ. In the case of the evaporation of neutral atoms—for example, atoms of oxygen from adsorbed films on heated tungsten filaments—the rate of evaporation is much more nearly proportional to θ.

In studies of the surface tensions of organic liquids (2) (17) and of the properties of adsorbed films of organic substances on water (3) (4) and of oil films on water, the principle of independent action has proved itself particularly useful. It gives immediately a simple reason for believing that these films should rarely be more than one molecule in thickness; or rather, that if they are more than one molecule in thickness, their properties will be markedly different from those of films in which the surface is not completely covered with a single layer. The theory also gives immediately reasons for believing that adsorbed films of many organic substances on water will consist of orientated molecules. Thus the area on a water surface occupied by molecules of the various fatty acids is dependent on an interaction between the carboxyl group and the water, and is independent of the length of the hydrocarbon chain. This simple result, proved by experiment, demonstrates that the molecules are orientated so that the carboxyl group is in contact with the water, leaving the hydrocarbon tails to form a layer above the carboxyl group which will have the properties characteristic of a liquid hydrocarbon.

The theory is equally applicable in pure organic liquids. The total surface energies (surface tension extrapolated to the absolute zero) of hexane and of hexyl alcohol are practically identical. This is readily explained by the orientation of the molecules which prevents the hydroxyl groups from coming in contact with the surface, so that in both cases the actual surface is that of a pure hydrocarbon.

Studies of the surface tension of aqueous solutions of various aliphatic compounds in water prove that in concentrated solutions the surface becomes covered with a closely packed monomolecular film consisting of orientated molecules like those in oil films. With sufficiently dilute solutions, however, the amount of substance adsorbed in the surface is not enough to cover the whole surface with closely packed molecules. Under these conditions, the hydrocarbon chain lies flat in the water surface and the energy needed to transfer any molecule from the surface to the interior increases by a definite amount for each additional CH_2 group in the hydrocarbon chain. This is an excellent example of the application of the principle of independent surface action, each CH_2 group producing its effect independently of the others.

Similar views prove useful in studies of many other properties of matter. Consider, for example, jellies made by amounts of gelatin or soaps in concentrations less than 1 per cent by weight. The elasticity proves the existence of a continuous frame-work of molecules in contact, extending throughout the liquid. The time of relaxation of such jellies serves as a measure of the rate at which the molecules which form the chains separate or evaporate from one another. Guided by these views, I made some experiments, over ten years ago, to determine the diameters of the cross sections of the fibers or rods that must be the elements of the rigid framework. For this purpose I made up some dilute gelatin jellies on filter paper and measured the rate at which water could be forced through the jellies by applying a definite pressure. By a modification of Stokes' law which gives the rate of fall of small spheres in liquids, it was possible to calculate the force necessary to move small cylinders of various diameters through a liquid. This law was then checked experimentally by measuring the rate at which water passed through a column of glass-wool having fibers of known size. Applying this law to the case of the motion of water through a gelatin jelly, it was thus possible to calculate the size of the fibers. Only rough experiments were made, but the results showed clearly that the diameter of the fibers was approximately 10^{-7} cm.

I believe that there is real justification for dealing with molecules of this character, at least as a first approximation, as though they followed the same laws as bodies of large size, such as the fibers of glass-wool. Einstein showed, years ago, that Stokes' law could be used, approximately, for the study of the rate of migration of ions through water solutions. I believe that a thorough quantitative study of the forces necessary to drive water through various jellies should give much valuable information as to the structure of these jellies.

Very useful pictures of the mechanism involved in the viscosity of liquids and of diffusion in liquids and solids may be had by considering that molecules in contact exist in two states: one in which the surfaces are rigidly connected, the other in which they are entirely free to move. The behavior of the molecules is thus analogous to that of a gas condensing on a solid; the molecules of the gas strike the surface, remain adsorbed for a certain time, and then evaporate off again. Applying this conception to molecules in liquids, we see that the motion of the molecules past each other, involving viscosity and diffusion, depends upon the relative times during which the molecules are in this rigid, or in this mobile contact. These times can be calculated from an equation of the Boltzmann type in terms of the energy difference between the two states. This theory accounts for the frequent occurrence of temperature coefficients of viscosity and diffusion, which agree with the Boltzmann equation. It seems also to account for the fact that the viscosity of different members of a series of hydrocarbons increases in geometrical proportion to the length of the chain. It would seem that the principle of independent surface action should afford a means for the development of a simple theory of viscosity which would take fully into account the shapes and sizes of the molecules and of the different chemical groups contained in the molecules.

The principle has also found many applications in connection with the mechanism of heterogeneous chemical reactions. The interaction of oxygen and hydrogen and of carbon monoxide and oxygen at low pressures in contact with a heated platinum filament (18) has shown that equations which are based directly on this principle are in excellent agreement with the experimental results over very wide ranges of pressure and temperature. For example, the experiments showed that at low temperatures the reaction velocity was accurately proportional to the partial pressure of oxygen and inversely proportional to the pressure of carbon monoxide. This behavior could be completely accounted for by assuming that the rate of reaction was determined by the rate at which oxygen molecules could reach holes in the films of adsorbed carbon monoxide which were left by evaporation of carbon monoxide molecules, or which were formed by the removal of the carbon monoxide by the oxygen which reached these holes. The poisoning effect of the carbon monoxide was due to the fact that the opportunity for the oxygen to reach the holes was decreased if the carbon monoxide molecules were able to fill up the holes before the oxygen arrived. It seems difficult to reach quantitative agreement with these experiments except by the application of the principle of independent surface action.

The interaction of hydrogen and oxygen in contact with tungsten filaments at temperatures ranging from 1500° to 2500°K is another illustration of a similar kind. Oxygen acts to form WO_3 at a rate proportional to the oxygen pressure (19). Oxygen atoms *in the adsorbed oxygen film* do not react with one another and with the tungsten to form WO_3 even at the highest temperatures. At 1500°K the life of oxygen atoms on the surface is of the order of years; at 1860°K it is about 25 minutes; and at 2070° K it is 15 seconds. When the atoms leave the films at the higher temperatures they do so as free atoms, not as molecules. Thus, even in the presence of minute pressures of oxygen, the tungsten surface is practically completely covered with a single layer of oxygen atoms. Oxygen molecules which strike this surface condense on it, but evaporate from this second layer at a relatively high rate; but while thus adsorbed, they move freely over the surface and are able to fill up any holes that form in the first layer. Also the molecules, while adsorbed in the second layer, have a certain probability of interacting with those of the first layer and with the underlying tungsten to form WO_3, and the holes thus formed by the removal of oxygen from the first layer are soon filled up by the migration of the molecules of the second layer.

Hydrogen molecules are not able at any temperature to react directly with the oxygen in either of the first or second layers (10), but if they reach the tungsten at one of the holes in the first layer, they react immediately with the adjacent oxygen. Thus when the oxygen pressure falls to a certain low critical value, the hydrogen completely removes all the oxygen from the surface, and it does this suddenly. The hydrogen which then strikes the film is dissociated into atoms to an extent that depends upon the temperature, and the atomic hydrogen formed goes to the bulb and reacts with the WO_3 which has previously been deposited there.

This theory which can readily be stated quantitatively appears to be in complete agreement with all the experimental facts, so that again we find support for the principle of independent surface action.

The molecules in adsorbed films on solutions of organic substances in water are frequently in a state of a two-dimensional gas. Oil films on water may exist as solid or liquid films. In the case of so-called expanded films (12), the heads of the molecules act as a two-dimensional gas, while the tails form a two-dimensional liquid. The molecules of oils adsorbed on solids, such as those that are responsible for some of the lubricating properties of oils, and those involved in the phenomena of flotation of ores, usually show little or no tendency to move over the surface. In other words, the molecules appear to be attached rigidly to the surface.

Many of the equations that were developed in the quantitative studies of the velocities of heterogeneous reactions assumed that bare spots on the surfaces were distributed over the surface according to statistical laws. Such statistical distribution would not occur unless the molecules possessed a certain degree of mobility over the surface, for the molecules that are removed by the reaction are those that are adjacent to holes already existing. Volmer and others have shown experimentally that adsorbed atoms frequently possess great mobility even on solid surfaces and thus act like two-dimensional gases of high viscosity.

I believe that the principle of independent surface action will be useful in studying many properties of organic substances which have hitherto been too complicated to be treated quantitatively. Within recent years I have made some attempts of this kind.

When a liquid is separated into two parts, along a surface having an area of 1 sq. cm., two new surfaces with a total area of 2 sq. cm. are formed. The surface tension or free surface energy measures the work done per unit area in forming the new surfaces. The total surface energy γ, which is equal to the free surface energy extrapolated back to the absolute zero, represents the total energy change per unit area. For all the pure hydrocarbons, such as pentane and nonane, γ is equal to about 48 ergs cm.$^{-2}$ The fact that this value is practically independent of the length of the hydrocarbon chain proves that the surface forces are very nearly uniform over the whole of the hydrocarbon molecule.

When a hydrocarbon, such as hexane, evaporates, molecules pass from the interior of the liquid into the vapor. If we consider a drop of hexane liquid to be removed from a large volume of the liquid into the free space above it, the work that would be needed to form this drop would be equal to $S\gamma$ where S is the surface area of the drop. Since we are regarding molecules as having surfaces possessing certain properties, we may say that the work necessary to remove a single molecule of hexane from the liquid, which is the latent heat of evaporation per molecule, will also be equal to $S\gamma$, where S is now the surface area of the molecule and γ is the surface energy of the molecule per unit area.

The molecular surface S for the molecule of vapor may be calculated from the molecular volumes (molecular weight divided by density), assuming the surfaces to be the same as in the case of closely packed spheres. This assumption would probably be quite accurate for large molecules, but would be only a rough approximation in the short chain hydrocarbons. From the known values of the latent heats of evaporation, the values of γ can then be calculated. Practically all of the normal hydrocarbons, with the exception of methane, give the value $\gamma = 34 \pm 1$ ergs cm.$^{-2}$. This value is of the same order of magnitude as the value 48 found from measurements of surface tension. The fact that γ is found to be constant proves that the work done in removing molecules from the liquid to the vapor phase is strictly proportional to the molecular surface. In other words, the latent heat of evaporation is proportional to the two-thirds power of the molecular volume.

This theory can readily be extended to cover the case of the heats of evaporation of the various aliphatic alcohols. If S is the total surface of the molecule of vapor, then aS is the surface of the head of the molecule (hydroxyl group) while cS is the area of the tail (hydrocarbon chain). We may let γ_a and γ_c represent the surface energies per unit area of the heads and tails respectively when the molecule is in the vapor phase. Thus $Sa\gamma_a$ is the total energy of the head and $Sc\gamma_c$ the total energy of the tail.

If the molecules of alcohol in the liquid phase were arranged at random, that is, if they did not orientate each other appreciably, and did not tend to form clusters (segregation), then it may readily be shown that the total interfacial surface energy in the liquid between the hydroxyl groups and the hydrocarbon chains will be $Sac\gamma_{ac}$, where γ_{ac} is the interfacial surface energy per unit area. We should therefore be able to calculate the latent heat of evaporation, λ, from the difference between the energies in the vapor and liquid phases.

$$\lambda = S(a\gamma_a - ac\gamma_{ac} + c\gamma_c)$$

If we take $\gamma_a = 193$, $\gamma_c = 34$, and $\gamma_{ac} = 34$, we get excellent agreement between the observed latent heats of evaporation and the structures of most monobasic alcohols. We have already seen that γ_c is equal to 34 as the value found for the evaporation of pure hydrocarbons. The value $\gamma_{ac} = 34$ was found as a result of experiments on the vapor pressures of mixtures of alcohol and water. The interfacial energy between water and a hydrocarbon is about 59, so that the value 34 is of the right order of magnitude. The surface energy of water is 117, but this naturally represents the surface energy of the least active part of the water molecule, whereas the energy γ_a equal to 193 corresponds to the most active part of the hydroxyl group so that this value also appears reasonable.

In the case of the alcohols having very long hydrocarbon chains another effect can be clearly seen from the experimental results. In the molecule of vapor the hydroxyl group is able to bury itself at least partially among the coils of the hydrocarbon tail, so that the surface energy of the vapor molecule decreases considerably, beginning with chains of five or six carbon atoms in length. With shorter chains than this, the hydroxyl group is probably fully exposed. Particularly interesting results which are in good agreement with the principle of independent surface action are found in the case of dibasic and tribasic alcohols. The heat of evaporation depends to a great extent on whether the separate hydroxyl groups are able to come into contact with each other in the molecule of vapor and thereby decrease the surface energy.

The theory can readily be extended to calculate the partial vapor pressures of binary solutions. The complete theory, taking into account orientation and segregation of molecules within the liquid, would be very complicated, but in many cases where the forces between molecules are not too strong, these effects can be neglected in a first approximation. Assuming then a random orientation and distribution of the molecules, the total surface energy per molecule in a solution of any given concentration in terms of interfacial surface energies, such as γ_{ac}, and surface fractions, such as a and c, the work done in transferring a molecule from a liquid to a vapor phase can then be calculated, and thus by applying the Boltzmann equation, it is possible to calculate the deviations from Raoult's law. Thus, the partial pressure of any liquid in a binary mixture is given by

$$p_A = AP_A \exp (\varphi S_A \beta^2/kT)$$

where p_A is the partial pressure of the substance A, the total pressure of the pure component A is P_A; the mole fraction of the component A is represented in this equation by A. The quantity S_A is the surface area per molecule of area; φ is a constant characteristic of the binary mixture but independent of the concentration of the components, which can be calculated in terms of such quantities as a, c, γ_{ac}, etc. The quantity β may be called the surface fraction of the component B in the binary mixture of A and B. It corresponds to the ordinary conception of mole fractions but is expressed in terms of the relative surfaces of the molecules instead of the numbers of the molecules. Thus

$$\beta = BS_B/(AS_A + BS_B)$$

This equation with only one adjustable constant, φ, apparently agrees in general better with experimental data than a somewhat similar equation with two adjustable constants derived by van Laar on the basis of thermodynamical considerations.

C. P. Smyth has recently used this equation in connection with his own measures of the vapor pressures of binary mixtures. The agreement, in most cases, is fairly good, but, as is to be expected in the case of more polar molecules, mixtures of alcohols with water show considerable deviations. It is probable that these can in large part be taken into account by developing the theory further to allow for orientation and segregation of the molecules within the liquid.

Views of the type which I have been discussing may thus be applied quantitatively, often with considerable accuracy, in studying the interactions between molecules of organic substances. The energy relations based on the conception of surface forces between molecules, together with the Boltzmann equation, frequently permit decisions to be made as to the mechanism of various surface phenomena. For example, in expanded films of oils on water it has often been assumed that the molecules could remain erect on the surface without touching one another. Simple energy considerations of the kind which we have been using indicate immediately that this is impossible. The tails of the molecules must remain in contact with each other in the case of long chains, but with shorter chains, the molecules may separate but must then lie flat upon the surface of the water. The principle of independent surface action affords one of the greatest safeguards against the setting up of impossible hypotheses.

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Chapter Eleven

ISOMORPHISM, ISOSTERISM AND COVALENCE

I HAVE DESCRIBED a theory of valence which I have called the octet theory.[1] This theory is based upon and is essentially an extension of G. N. Lewis' theory of the "cubical atom." [2] According to this theory each bond between adjacent atoms in organic compounds corresponds to a pair of electrons held in common by the two atoms. Since in other types of compounds the number of pairs of electrons held in common is not always the same as the number of valence bonds that have usually been assumed I proposed that the number of pairs of electrons which any given atom shares with the adjacent atoms be called the covalence of that atom. It was then shown that the covalence of carbon is always 4, that of nitrogen is usually 3 or 4, while that of oxygen is 1, 2 or sometimes 3, etc.

The octet theory indicates that the number and arrangement of electrons in the nitrogen molecule, the carbon monoxide molecule, and the cyanogen ion, is the same, and it was shown in fact that the physical properties of nitrogen and carbon monoxide are remarkably alike.

A similar relationship was found to exist between nitrous oxide and carbon dioxide and again between cyanic and hydronitric acid.

The following data, taken from Landolt-Börnstein's tables and Abegg's handbook, show the extraordinary agreement between physical properties of carbon dioxide and nitrous oxide:

Both gases form hydrates, $N_2O.6H_2O$ and $CO_2.6H_2O$. The vapor pressure of the hydrate of nitrous oxide is 5 atm. at $-6°$, whereas the hydrate of carbon dioxide has this vapor pressure at $-9°$. The heats of formation of the two hydrates are given, respectively, as 14900 and 15000 calories per mol. The surface tension of liquid nitrous oxide is 2.9 dynes per cm. at 12.2°, while carbon dioxide has this same surface tension at 9.0°.

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[1] A simpler exposition of the theory and its applications is given by Elwood Hendrick, *Met. Chem. Eng., 21,* 73 (1919), July 15th; Langmuir, *Jour. Frank. Inst., 187,* 359 (1919) ; *Jour. Amer. Chem. Soc., 41,* 868–934 (1919) ; *Proc. Nat. Acad. Sci., 5,* 252 (1919).

[2] G. N. Lewis, *Jour. Amer. Chem. Soc., 38,* 762 (1916).

Thus nitrous oxide at any given temperature has properties practically identical with those of carbon dioxide at a temperature 3° lower.

	N_2O.	CO_2.
Critical pressure, atm	75	77
Critical temp	35.4°	31.9°
Viscosity at 20°	148×10^{-6}	148×10^{-6}
Heat conductivity at 100°	0.0506	0.0506
Density of liquid at —20°	0.996	1.031
Density of liquid at +10°	0.856	0.858
Refractive index of liquid, D line, 16°	1.193	1.190
Dielectric constant of liquid at 0°	1.598	1.582
Magnetic susceptibility of gas at 40 atm., 16°	0.12×10^{-6}	0.12×10^{-6}
Solubility in water 0°	1.305	1.780
Solubility in alcohol at 15°	3.25	3.13

There is one property, however, which is in marked contrast to those given above. The freezing point of nitrous oxide is $-102°$, while that of carbon dioxide is $-56°$. This fact may be taken as an indication that the freezing point is a property which is abnormally sensitive to even slight differences in structure. The evidences seem to indicate that the molecule of carbon dioxide is more symmetrical, and has a slightly weaker external field of force than that of nitrous oxide. Such differences could easily be produced by the difference in the charges on the kernels, and may also be taken as evidence that the structure of nitrous oxide is represented by $N = N = O$ rather than $N = O = N$.

Compounds showing a relationship to one another like that between carbon dioxide and nitrous oxide will be called isosteric compounds, or isosteres. These terms, however, are not to be restricted to chemical compounds but are applicable to chemical radicals or to groups of atoms which hold pairs of electrons in common. A comolecule is defined as a group of atoms held together by pairs of electrons shared by adjacent atoms. Comolecules are thus isosteric if they contain the same number and arrangement of electrons. The comolecules of isosteres must, therefore, contain the same number of atoms. The essential differences between isosteres are confined to the charges on the nuclei of the constituent atoms. Thus in carbon dioxide the charges on the nuclei of the carbon and oxygen atoms are 6 and 8, respectively, and there are $2 \times 8 + 6 = 22$ electrons in the molecule. In nitrous oxide the number of charges on the nitrogen nuclei is 7, but the total number of electrons in the molecule is again $2 \times 7 + 8 = 22$. The remarkable similarity of the physical properties of these two substances proves that their electrons are arranged in the same manner.

According to the object theory we may expect the following types of isosteres:

TABLE I

List of Isosteres[*]

Type.	
1	H^-, He, Li^+
2	O^{--}, F^-, Ne, Na^+, Mg^{++}, Al^{+++}
3	S^{--}, Cl^-, A, K^+, Ca^{++}
4	Cu^+, Zn^{++}
5	Br^-, Kr, Rb^+, Sr^{++}
6	Ag^+, Cd^{++}
7	I^-, Xe, Cs^+, Ba^{++}
8	N_2, CO, CN^-
9	CH_4, NH_4^+
10	CO_2, N_2O, N_3^-, CNO^-
11	NO_3^-, CO_3^{--}
12	NO_2^-, O_3
13	HF, OH^-
14	ClO_4^-, SO_4^{--}, PO_4^{---}
15	ClO_3^-, SO_3^{--}, PO_3^{---}
16	SO_3, PO_3^-
17	$S_2O_6^{--}$, $P_2O_6^{----}$
18	$S_2O_7^{--}$, $P_2O_7^{----}$
19	SiH_4, PH_4^+
20	MnO_4^-, CrO_4^{--}
21	SeO_4^{--}, AsO_4^{---}

All the comolecules given under any one type are isosteric with one another.

When isosteric comolecules are also isoelectric, that is when they have the same total charge on the comolecules, all their physical properties should be closely similar. In Table I the only pairs of comolecules which are also isoelectric are: (8) N_2 and CO, (10*a*) CO_2 and N_2O and (10*b*) N_3^- and NCO^-.

I have already pointed out that the physical properties of the first two pairs of substances (8 and 10*a*) furnish proof of the similarity of structure predicted by the octet theory, and show the usefulness of the conception of isosterism.

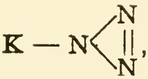
The isosterism of the cyanate and trinitride ions applies of course also to compounds derived from them. Thus we should expect HNCO and HN_3 to be isosteric as well as pairs of compounds such as KNCO–KN_3 $Ba(NCO)_2$–$Ba(N_3)_2$, etc.

There are, unfortunately, very few data on the physical properties of cyanates and trinitrides. Both cyanic and hydronitric acids are liquids at 0° and both explode on heating. Apparently the freezing point of cyanic acid has not been determined. In a general way the solubilities of the salts of these two acids are known to be similar; the potassium and the barium salts of both acids are readily soluble in water, while the lead and silver salts are very difficultly soluble.

Groth [3] gives the following crystallographic data for anhydrous potassium cyanate and trinitride. Both belong to the tetragonal system. The ratio of the axes $a:c$ is 1:0.5766 for the cyanate and 1:0.5798 for the trinitride. Both have "strong negative double refraction." The most common faces of both crystals are given as C (001) and O (111). Cleavage was not observed in either case. No other data are given by Groth from which a comparison of cyanates and trinitrides can be made.

From the octet theory and the above data it is therefore safe to predict that the physical properties of the salts of cyanic and hydronitric acids will be found to be practically identical. This resemblance should be at least as close as that between nitrous oxide and carbon dioxide and should cover solubility in water, in alcohol, etc., density in crystalline form and in solutions, viscosity of solutions, optical and magnetic properties, electric conductivity of solutions, etc. The densities should be alike because the molecular weight of N_3 is the same as that of NCO.

The available experimental data, although meager, are sufficient, I think, to show the complete isomorphism of cyanates and trinitrides. The similarity of structure thus follows directly from Mitscherlich's rule. These experimental data furnish direct evidence against such structural formulas as



$$K-N=N\equiv N, \quad K-O-C\equiv N,$$

but strongly support the octet theory structures:

$$K^+(N=C=O)^- \quad \text{and} \quad K^+(N=N=N)^-$$

These formulas show that the covalence of potassium is zero; the nitrogen and oxygen in the cyanate are dicovalent, while in the trinitride one of the nitrogens is quadricovalent and the other two are dicovalent. These data, as far as they go, thus constitute experimental proof of the octet theory of valence. Further experimental work on the physical properties of cyanates and trinitrides is highly desirable.

The octet theory also indicates that diazomethane should have the structure $H_2C=N=N$ and should thus be isosteric with $H_2C=C=O$, a compound apparently not given in Beilstein. This compound should closely resemble diazomethane in all its physical properties such as freezing point, vapor pressure, viscosity, etc.

No direct comparison can be made of the physical properties of isosteres having different electric charges. Thus we should not expect sodium salts to resemble neon, even though the sodium ion is an isostere of the neon atom—the electric force around the ion is sufficient to account for the differences in physical properties.

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[3] P. Groth, "Chemische Krystallographie," Leipzig, Part I, 1906, Part II, 1908.

There is, however, another way in which the actual isosterism of co-molecules with different charges can be tested from experimental data. It is evident that if any two substances are very much alike in physical properties, then any isoelectric isosteres of these substances should show similarly close relationships with one another. For example, in Types 3 and 8 of Table I, we find argon and nitrogen resemble each other closely. Therefore the chlorine ion, isosteric with argon, should have a close resemblance to the cyanogen ion which is isosteric with nitrogen. The striking similarity of chlorides and cyanides is thus directly correlated with that between argon and nitrogen.

In an exactly similar manner the close relationship between potassium salts and ammonium salts can be derived from the similarity between the physical properties of argon and methane. For from Table I (Types 3 and 9) the potassium ion is isosteric with argon, while the ammonium ion is an isostere of methane. Of course the potassium ion and the ammonium ion are not isosteres of one another. The resemblance between potassium and ammonium salts is of a much lower order than that between truly isosteric substances such as nitrous oxide and carbon dioxide, or between salts of cyanic and hydronitric acids. The octet theory indicates in fact that the potassium ion is cubic in form, while the ammonium ion, like methane, must have a tetrahedral symmetry. This conclusion is in accord with the crystal structures of potassium chloride and ammonium chloride. Bragg[4] has found that in potassium chloride each potassium ion is surrounded by 6 equidistant chlorine ions, arranged just as if the crystal were built up of cubical potassium and chlorine ions with their faces in contact; but finds that ammonium chloride, although it crystallizes in the isometric system, is in no sense isomorphous with the other alkaline halides. Each ammonium ion is surrounded by 8 equidistant chlorine ions arranged like the corners of a cube about its center. This indicates that the tetrahedral ammonium ions force the chlorine ions to arrange themselves symmetrically with respect to the 4 faces or corners of the tetrahedron, while the cubical potassium ions permit the simpler cubic packing. Ammonium and potassium sulfates, however, are isomorphous, for the larger volume of the sulfate ion causes its influence to predominate over the slight differences between the forces around the two positive ions.

[4] W. H. Bragg and W. L. Bragg, "X-Rays and Crystal Structure," London, *1916*, pp. 95 and 158.

The nitrates and perchlorates of all metals are readily soluble and most of them are deliquescent. From this similarity of properties we may conclude that the other isosteres of Types 11 and 14 of Table I should be interrelated. Thus carbonates and sulfates should show a general resemblance to each other in their solubilities.

The smaller solubility of salts of divalent ions is, of course, due to the greater forces holding the divalent ions, making it more difficult for them to separate. The process of solution of salts involves, according to the octet theory, the separation of the ions. Thus sulfates and carbonates of most metals are difficultly soluble compared to the nitrates and perchlorates. Salts like lead and barium carbonates and sulfates in which both ions are divalent, are thus particularly difficultly soluble.

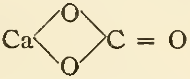
Boron nitride, which consists of tervalent ions, has still greater stability, and is infusible and insoluble in all solvents.

The observed differences between the ordinary properties of the differently charged isosteres are thus to be expected. But there is one property, namely crystalline form, which should depend on the arrangement of the electrons in substances rather than upon the magnitude of the forces between their atoms. By a comparison of crystal forms it should therefore be possible to obtain direct evidence of the similarity of the arrangement of the electrons in isosteric substances even if the charges on the comolecules are different.

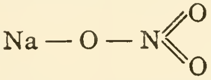
For example, since the sodium ion and the fluorine ion are isosteric and cubic in form, we should expect them to pack together in a crystal lattice in exactly the way that Bragg has found they do. The magnesium and oxygen ions, however, are also isosteric with the sodium and fluorine ions, so that we should expect magnesium oxide to have a crystal structure identical in form with that of sodium fluoride. According to Groth both substances are cubic, sometimes crystallizing as octahedra, and both show good cleavage parallel to the (100) plane. To answer the question thus raised, Dr. A. W. Hull has studied the X-ray patterns obtained with magnesium oxide and sodium fluoride and has thus recently found that the crystal structures of both substances are alike, except that the atoms in magnesium oxide are drawn closer together by the greater forces. Thus magnesium oxide and sodium fluoride should be looked upon as isomorphous. By the octet theory the covalences of all the atoms in these substances are zero, since they do not share electrons with each other. The isomorphism is thus in full accord with Mitscherlich's rule by which isomorphous substances should have similar structures. Since the ions O^{--}, F^{-}, Na^{+} and Mg^{++} are isosteric we should also expect that MgF_2 and Na_2O should be isomorphous. Groth states that sodium oxide has not been obtained in the form of well developed crystals. However, by Hull's method of X-ray analysis, substances can now be studied in powdered form so that we may hope to see whether in fact these two substances are isomorphous. Other pairs of substances which may be isomorphous are potassium chloride and calcium sulfide, potassium sulfide and calcium chloride, cuprous sulfide and zinc chloride, etc.

A still more interesting class of isomorphous substances which are predicted by the octet theory is that represented by sodium nitrate and calcium carbonate. Since the nitrate and carbonate ions are isosteric we should expect sodium nitrate and magnesium carbonate to be isomorphous, Na^+ and Mg^{++} being isosteric. As a matter of fact, both substances are given by Groth as trigonal scalenohedral with the ratio of the axes 1 :0.8297 and 1 :0.8095, respectively.

The practical identity in all the crystallographic properties of sodium nitrate and calcium carbonate has long been known. In Mitscherlich's early theory before clear ideas of valence were developed, no difficulty was experienced in regarding these two substances as isomorphous and as having similar structures. The theory of valence, however, gave formulas



and



so that they could no longer be regarded as of similar structure. It was necessary either to abandon Mitscherlich's rule or to re-define isomorphism so as to exclude cases of this kind. Therefore Kopp [5] and Retgers [6] regarded substances as isomorphous only when they are capable of forming *mixed crystals*. This effectually eliminated such cases as sodium nitrate and calcium carbonate because mixed crystals can naturally only be obtained when the solubilities of the two substances are not too widely different. The crystal form depends, of course, exclusively, on the arrangement of the atoms and the electrons in them, while the ability to form mixed crystals depends on both similarity of arrangement and on similarity in the magnitude of the forces acting between the atoms. Thus Kopp found a practical rule by which nearly all those cases inconsistent with the ordinary valence theory, could be excluded. In order to be isomorphous in Kopp's sense, two substances must have atoms which are not only linked together in the same manner, but also have the same number of available electrons in corresponding atoms.

T. V. Barker,[7] however, and a few other crystallographers have maintained that isomorphism should be used to denote similarity of crystal form. Barker pointed out a great many new cases of isomorphism between substances which according to the ordinary valence theory are not closely related. Among these he mentions as types KIO_4–$CaWO_4$; $KClO_4$–$BaSO_4$–KBF_4; K_2SO_4–K_2BeF_4; and $NaNO_3$–$CaCO_3$. He shows how these cases of isomorphism are inconsistent with the ordinary valence theory, but are in a general way in agreement with Werner's coördination theory.

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[5] *Ber.*, *12*, 868 (1879).

[6] *Z. physik. Chem.*, *3*, 497 (1889), and later papers in 1889 to 1896.

[7] *Trans. Chem. Soc.*, *101*, 2484 (1912).

By examining Table I it is evident that we should expect the following cases of isomorphism of the kind just considered:

TABLE II

Typical Cases of Isomorphism Based on Isosterism

Type. Table I.	
2	(*a*) NaF–MgO; (*b*) MgF_2–Na_2O
3	(*a*) KCl–CaS; (*b*) $CaCl_2$–K_2S
5	(*a*) $RbBr$–$SrSe$; (*c*) $SrBr_2$–Rb_2Se
7	(*a*) CsI–$BaTe$; (*c*) BaI_2–Cs_2Te
8	N_2–CO
10	$KNCO$–KN_3, etc.
11	(*a*) $NaNO_3$–$CaCO_3$; (*b*) KNO_3–$SrCO_3$
14	(*a*) $KClO_4$–$SrSO_4$; (*b*) $NaHSO_4$–$CaHPO_4$ (*c*) $KHSO_4$–$SrHPO_4$
15	(*a*) $NaClO_3$–$CaSO_3$; (*b*) $KHSO_3$–$SrHPO_3$
17	$Na_2S_2O_6$–$Ca_2P_2O_6$
18	$Na_2S_2O_7$–$Ca_2P_2O_7$
20	$RbMnO_4$–$BaCrO_4$
21	$MnSeO_4.2H_2O$–$FeAsO_4.2H_2O$

Sodium nitrate crystals resemble those of calcium carbonate a little more closely than those of magnesium carbonate, although the sodium ion is isosteric with the magnesium ion but not with the calcium ion. The molecular volume of sodium nitrate is nearer to that of calcium carbonate than that of the magnesium compound. The much larger forces in the compounds containing the divalent ions must tend to draw the atoms closer together. The substitution of the larger calcium ion in place of the magnesium ion offsets this difference, and this probably accounts for the closer resemblance between the sodium and the calcium compounds. This same relationship is noticed in other pairs of compounds. Since in these replacements calcium corresponds most nearly to sodium we should expect strontium to correspond to potassium and barium to rubidium. This is well borne out in every case. The following tables illustrate the cases of isomorphism corresponding to Types 11 to 21, shown in Table II, for which data are given by Groth. The pairs of substances at the head of each table are those given in Table II. The other substances are generally recognized as being isomorphous with one or the other members of these pairs.

TABLE III

NITRATES AND CARBONATES, TYPE 11 (*a*). TRIGONAL SCALENOHEDRAL

	a	:	c.	
$NaNO_3$	1	:	0.8297	
$CaCO_3$	1	:	0.8543	
$MgCO_3$	1	:	0.8095	
$MnCO_3$	1	:	0.8259	
KNO_3	1	:	0.8259	Stable above 128°

At high temperatures $RbNO_3$, $SrCO_3$ and $BaCO_3$ also give trigonal crystals. All these substances show strong negative double refraction and similar cleavage.

TABLE IV

NITRATES AND CARBONATES, TYPE 11 (*b*). ORTHORHOMBIC BIPYRAMIDAL

KNO_3	0.5910	1	0.7011
$SrCO_3$	0.6090	1	0.7237
$CaCO_3$	0.6228	1	0.7204
$BaCO_3$	0.5949	1	0.7413

Negative double refraction.

TABLE V

PERCHLORATES AND SULFATES, TYPE 14 (*a*). PERMANGANATES AND CHROMATES, TYPE 20. ORTHORHOMBIC BIPYRAMIDAL

	a.	b	c.		Cleavage.
$KClO_4$	0.7817	1	1.2793	*c*(001)	*m*(110)[1]
$SrSO_4$	0.7790	1	1.2800	*c*(001)	*m*(110)[1]
$RbMnO_4$	0.8311	1	1.3323	..	....
$BaCrO_4$	0.8231	1	1.3232	..	....
$RbClO_4$	0.7966	1	1.2879	*c*(001)	*m*(110)
$BaSO_4$	0.8152	1	1.3136	*c*(001)	*m*(110)[1]
$KMnO_4$	0.7972	1	1.2982	*c*(001)	*m*(110)[1]
$SrCrO_4$	0.9496	1	1.0352	..	....
$CsClO_4$	0.8173	1	1.2976	..	....
$CsMnO_4$	0.8683	1	1.3705	..	....
$CaSO_4$	0.8932	1	1.0008	..	....
NH_4ClO_4	0.7932	1	1.2808	..	....

Groth gives no data for the Types 15 (*a*), 15(*b*), 17 and 18 of Table II.

The results given in these tables afford the strongest kind of evidence for the octet theory of valence and prove that crystal form depends on the covalence of the atoms forming the substance rather than upon the valences given by the ordinary theory.

In every one of the cases where isomorphism is predicted by the octet

TABLE VI

SULFATES AND PHOSPHATES, TYPE 14 (*b*). TRICLINIC PINACOID

	a.	*b.*	*c.*	*α.*	*β.*	*γ.*
$NaHSO_4$[2]	0.6460	1	0.8346	85° 06′	88° 57′	86° 47′
$CaHPO_4$	0.6467	1	0.8244	84° 57′	89° 43′	85° 38′
$SrHAsO_4$	0.6466	1	0.8346	86° 32′	89° 14′	87° 56′

theory (see Table II), we find that the data available in Groth's "Chemische Kristallographie" indicate an almost complete identity of crystalline form. The agreement between the pairs of substances given in Table II is in fact usually rather better than among most of the classical examples of isomorphism. For example, the agreement of the ratios of the axes for potassium perchlorate and strontium sulfate (Table V) is much closer than among the various chlorates or among the sulfates. Sodium nitrate crystals (Table III) are more nearly like calcium carbonate than these are like magnesium carbonate. Potassium nitrate (Table IV) shows better agreement with strontium carbonate than calcium carbonate (aragonite) does with barium carbonate. Sodium hydrogen sulfate (Table VI) agrees slightly better (in axial angles) with calcium hydrogen phosphate than this does with strontium hydrogen arsenate.

In several of the cases in Table II we find that no data are given by Groth by which a comparison between the crystalline form of similarly constituted compounds can be made. For example (Type 15*a*), no anhydrous sulfites of divalent metals and no hydrated chlorates of univalent metals are given. Although sodium hydrogen sulfite is given, no phosphites of divalent metals have been measured.

It seems safe to predict that nearly all the remaining pairs of substances given in Table II will be found to be isomorphous when data become available. By Hull's method of X-ray analysis these comparisons are now possible even with powdered materials, so that most of the difficulties disappear that have heretofore prevented the accumulation of such data.

We have thus far considered cases in which the octet theory leads us to expect isomorphism not predicted by the ordinary theory of valence. Let us now consider those cases where the ordinary theory indicates isomorphism, but the octet theory does not. Examples of this kind are, (*a*) carbonates and sulfites, (*b*) chlorates and nitrates, (*c*) chlorates and metaphosphates.

According to the ordinary theory the sulfur in sulfites has a valence of

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[1] Incomplete cleavage.

[2] Axes *b* and *c* have been interchanged in order to correspond to those used to form the other compounds. Where the angles α, β, γ, were greater than 90° their supplementary angles were chosen.

TABLE VII

SULFATES AND PHOSPHATES, TYPE 14 (*c*). ORTHORHOMBIC BIPYRAMIDAL

	a.	b	c.
$SrHPO_4$[1]	0.8581	1	1.9431
$KHSO_4$	0.8609	1	1.9344

Both substances form 8- or 4-sided plates parallel to *c*(001) with (111) as the next most important face. The plane of the optic axis is (001).

4 like that of carbon in carbonates. In chlorates and nitrates the central atom is supposed to have a valence of 5. By the octet theory, however, the covalence of sulfur in normal sulfites is 3, while that of carbon in carbonates is 4. In chlorates the covalence of chlorine is 3, while in metaphosphates that of the phosphorus is 4. A great deal of effort has been expended by chemists and crystallographers to prove cases of isomorphism between nitrates and chlorates. Groth says that carbonates and sulfites should be expected to be isomorphous and recommends that much more work be done in a comparative study of these salts—especially he advises attempting to prepare mixed crystals. In spite of this effort and the belief

TABLE VIII

SELENATES AND ARSENATES, TYPE 21. ORTHORHOMBIC BIPYRAMIDAL

	a.	b.	c.
$MnSeO_4.2H_2O$	0.8849	1	0.9959
$FeAsO_4.2H_2O$	0.8658	1	0.9541

Plane of the optic axis (100) in both.

[1] The measurements on $SrHPO_4$ and on $CaHPO_4$ given in Table VI were made by Schulten, *Bull. Soc. franç mineral 27,* 120 (1904).

According to Groth the ratio of the axes for $SrHPO_4$ was found to be 0.6477:1:0.8581 and the only faces measured were (100), (133), (203), (130), (230), (010). Groth states that the chosen orientation of the $CaHPO_4$ crystals was adopted because of the relationships to those of $SrHPO_4$.

For the substance $BaHPO_4$ which Schulten finds to be orthorhombic he gives the ratios 0.7133:1:0.8117, and considers that these ratios are related to those given above for $SrHPO_4$ (see Groth, p. 815) although the crystals are of "entirely different form." These facts make it clear that Schulten chose for this orthorhombic crystal the axial ratio $a:b::0.6477:1$ simply to make this ratio agree with $a:b::0.6467:1$ which he had obtained for the *triclinic* crystals of $CaHPO_4$ and which he supposed isomorphous with $SrHPO_4$ notwithstanding that they belonged to a different crystal system. If we multiply the *a* intercept 0.6477 by 3 and then interchange the *a* and *c* axes we obtain the ratios given above in Table VII. The crystal faces which Schulten measured should thus be denoted by (100), (111), (201), (110), (210), and (010) instead of the absurd set of faces (100), (133), (203), (130), (230) and (010) given by Schulten. There is thus ample internal evidence for making this change in Schulten's data. We may conclude that there is no similarity in the ratios between the axes of the triclinic $CaHPO_4$, the orthorhombic $SrHPO_4$ and the orthorhombic $BaHPO_4$, but they represent 3 distinctly different crystal types.

of chemists in the similarity of the constitutions of these compounds, there seem to be no convincing data indicating similarity of crystalline form in these cases. For example, Groth points out that potassium hydrogen carbonate and potassium hydrogen sulfite both belong to the monoclinic system, and that their crystals have the same habit. An examination of the data shows that both form crystals which are elongated in the direction of the *b*-axis. The following crystallographic data, however, prove that the substances are very far from isomorphous:

	a.	*b.*	*c.*	*β.*
$KHCO_3$	2.6770	1	1.3115	103° 25′
$NaHCO_3$	0.7645	1	0.3582	93° 19′
$KHSO_3$	0.9276	1	2.2917	94° 46′

The ratios of the axes could hardly be more different, and there is a difference of 9° in the inclination of the axes. The sodium acid carbonate is also monoclinic but has quite different constants from either of the other compounds. No other anhydrous sulfites are given by Groth.

The following hydrated sulfites and carbonates given by Groth are the only ones that are comparable in constitution. Ammonium sulfite, $(NH_4)_2SO_3.H_2O$, is monoclinic while sodium carbonate, $Na_2CO_3.H_2O$, is orthorhombic. The compound $Na_2CO_3.7H_2O$ is orthorhombic but $Na_2SO_3.7H_2O$ is monoclinic. Finally, $MgCO_3.3H_2O$ crystallizes in the orthorhombic system, while $MgSO_3.3H_2O$ is "ditrigonal pyramidal." All of the available crystallographic data thus seem to indicate conclusively that sulfites and carbonates do not have similar constitutions.

The chlorates and nitrates usually have different crystalline forms, but in many cases it has been found possible to make mixed crystals containing as much as 10 or 15% of one or the other of the constituents. Sodium chlorate crystallizes in the cubic system isomorphous with sodium bromate, while sodium nitrate is trigonal. This form of sodium chlorate is normally produced either from aqueous solution or by cooling the molten mass. By slow evaporation of a strongly supersaturated aqueous solution it is possible to obtain sodium chlorate in a trigonal form with angles very much like those of sodium nitrate, and also having negative double refraction like that of sodium nitrate; this trigonal form of sodium chlorate is very unstable, and soon goes over into the cubic form even at room temperature. It was found possible to prepare mixed crystals of sodium nitrate and chlorate containing as much as 22.5% of the chlorate. An unstable monoclinic form of sodium chlorate has also been prepared.

Potassium chlorate crystallizes only in the monoclinic form with axes inclined 109°, while potassium nitrate is orthorhombic. Notwithstanding the fact that the crystals belong to different systems, Groth states that potassium chlorate and sodium nitrate closely resemble each other. He does not believe that mixed crystals can be formed because the molecular volumes are so different. However, monoclinic mixed crystals of potassium chlorate and potassium nitrate up to 15% of the nitrate have been obtained, as well as orthorhombic mixed crystals, with 25% of the chlorate. This is considered to denote similarity of structure, notwithstanding the complete difference of crystal form between potassium nitrate and chlorate. Silver chlorate and bromate are tetragonal while silver nitrate is orthorhombic. The chlorate also forms cubic crystals isomorphous with sodium chlorate. Silver chlorate thus shows no resemblance to the nitrates.

Anhydrous calcium, strontium, and barium nitrates crystallize in the cubic system, but strontium chlorate $Sr(ClO_3)_2$ is orthorhombic with axial ratios, 0.9174:1:0.6003. It also exists in 3 other modifications, no one of which is cubic. However, even here it has been possible to make mixed crystals containing 7 to 12% of chlorate.

The salts $Mg(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$, are monoclinic, the nickel and cobalt salts being isomorphous with each other but not with the magnesium salt. On the other hand, the corresponding chlorates of nickel and cobalt, $Ni(ClO_3)_2.6H_2O$, etc., and the bromates of magnesium, nickel, cobalt and zinc, $Mg(BrO_3)_2.6H_2O$, etc., are cubic. Only in one instance were mixed crystals obtained: $Zn(BrO_3)_2.6H_2O$ and $Co(NO_3)_2.6H_2O$ crystallizing together as cubic crystals.

Looking back over this comparison of chlorates and nitrates we see that among the 20 compounds considered (belonging to 5 different crystal systems), there is only one instance, namely that of sodium nitrate and the unstable trigonal modification of sodium chlorate, in which corresponding nitrates and chlorates even belong to the same system.

This evidence seems sufficient to prove that nitrates and chlorates have fundamentally different constitutions. A careful study of the trigonal form of sodium chlorate should be made, preferably by the X-ray method, to determine if its structure is actually like that of sodium nitrate. If it turns out to be so, it is probably to be explained as a very unusual form in which two of the electrons in the atoms constituting the chlorate ion become unavailable, perhaps by being imprisoned within one of the octets. Under such conditions the chlorate ion might become "pseudo-isosteric" with the nitrate ion, so that the chlorine atom might then act with a covalency of 4.

There are no available data by which to test isomorphism between chlorates and metaphosphates.

These considerations show that the ordinary valence theory not only fails to predict cases of isomorphism which do exist (for example, potassium chlorate and strontium sulfate) but predicts isomorphism (sulfites and carbonates) where none exists. The octet theory does not fail in either of these ways. I have used the word isomorphism as expressing a close resemblance in crystallographic data. The data given in the cases of the nitrates and chlorates show conclusively in my mind that the formation of

	a.	b.	c.	β
A. Monoclinic.				
$CuTiF_6.4H_2O$	0.7471	1	0.5564	104° 9′
$CuCbOF_5.4H_2O$	0.7627	1	0.5629	103° 20′
$CuWO_2F_4.4H_2O$	0.7648	1	0.5629	103° 14′
B. Monoclinic.				
K_3HSnF_8	0.6277	1	0.4928	93°
K_3HCbOF_7	0.6279	1	0.4900	93° 14′
C. Orthorhombic.				
$K_2SnCl_4.2H_2O$	0.6852	1	0.7586	....
$K_2FeCl_5.H_2O$	0.6911	1	0.7178	....
D. Monoclinic.				
$MnCl_2.4H_2O$	1.1525	1	0.6445	99° 25′
$BeNa_2F_4$	0.9913	1	0.6929	99° 20′
E. Tetragonal.				
YPO_4	..	1	0.6177	....
$ZrSiO_4$	..	1	0.640	....
Sn_2O_4	..	1	0.6726	....
F. Tetragonal.				
KIO_4	..	1	1.5534	....
$CaWO_4$	..	1	1.5268	....
$KOsO_3N$	..	1	1.6319	....
$KRuO_4$		1	1.6340	....
G. Orthorhombic.				
$KClO_4$	0.7817	1	1.2792	....
$BaSO_4$	0.8152	1	1.3136	....
KBF_4	0.7898	1	1.2830	....
H. Orthorhombic.				
K_2SO_4	0.5727	1	0.7418	....
K_2BeF_4	0.5708	1	0.7395	....
$[N(CH_3)_4]_2HgCl_4$	0.5766	1	0.7893	....
$ZnI_2.4NH_8$	0.5754	1	0.7922	....
I. Monoclinic.				
$(NH_4)_2SeO_4$	1.8900	1	1.1987	115° 29′
Cs_2HgI_4	1.3155	1	0.9260	110° 4′
(the cleavage is the same)				
J. Trigonal.				
$NaNO_3$	..	1	0.8297	....
$CaCO_3$	..	1	0.854	....
K.				
Albite $NaAlSi_3O_8$	Are closely isomorphous.			
Anorthite $CaAl_2Si_2O_8$				

crystals often occurs when there is no close resemblance in crystal structure. It seems therefore that this criterion should not be used to indicate similarity in chemical constitution. The question of course arises: how many other cases of mixed crystals could be found if the same effort were expended in looking for them among other types of compounds.

Let us not consider in more detail the cases of isomorphism given by Barker:

The theory of chemical structure given in the recent paper in the *Jour. Amer. Chem. Soc.* is in full accord with these cases of isomorphism, and affords an explanation of them. In the second method [11] of regarding complex compounds with a coördination number of 6 or more, it was explained how groups such as chloride ion, ammonia, water, etc., could be held by electrostatic attraction to a positively charged central atom. We have already seen how in typical octet compounds such as potassium sulfate, etc., oxygen is unicovalent and may thus be replaced by fluorine without involving a change in the crystalline structure. The compounds in Groups A. B. G, and I are examples of this kind where fluorine, iodine or oxygen replace one another. Group C gives an illustration of a positive central ion (Sn^{++} or Fe^{+++}) surrounded by 6 other groups (Cl^- or H_2O) forming a complex ion. The H_2O group in the first compound replaces one of the chlorine ions of the second.

The compounds of Groups D and H afford interesting illustrations of the replacement of negative by positive ions and *vice versa* in a manner exactly analogous to that of Na_2O–MgF_2, etc., of Table II. Thus in $BeNaF_4$ the two sodium ions replace the two chlorine ions of the $MnCl_2.4H_2O$, the beryllium ion replaces the manganese ion and the fluorine ions replace the water comolecules. Similarly, in comparing $ZnI_2.4NH_3$ with K_2SO_4 we see that the iodide ions have replaced the potassium ions. This is evident if we apply the octet theory in the ordinary way to the compound $ZnI_2.4NH_3$. The number of available electrons in the atoms of this compound is $e = 48$. We place $n = 7$, assuming that the zinc, iodine and nitrogen atoms all form octets. We then find from the octet equation ($2p = 8n - e$) the value $p = 4$, from which we find the structure $I_2^-[Zn(NH_3)_4]^{++}$, in which each nitrogen atom is quadricovalent and shares a single pair of electrons with the octet of the zinc atom. The constitution is thus exactly analogous to $K_2^+SO_4^{--}$, for in this case the quadricovalent sulfur atom shares a single pair of electrons with each of the oxygen atoms.

If we apply the octet theory in the same way to $BeNa_2F_4$ and $MnCl_2.4H_2O$ we place for both compounds $e = 32$, $n = 5$ and find $p = 4$. This gives the structures

$$[Mn(OH_2)_4]^{++}Cl_2^- \quad \text{and} \quad [BeF_4]^{--}Na_2^+.$$

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[11] *Jour. Amer. Chem. Soc.*, *41*, 868 (1919) beginning middle of p. 930.

The manganese and beryllium atoms are thus quadricovalent, the water and ion share single pairs of electrons with the central atom. In the first compound the oxygen is tercovalent. The substitution of water or ammonia for fluorine or oxygen in these compounds is analogous to the substitution of K^+ in K_2SO_4 by NH_4^+.

The same explanations apply to the other examples cited by Barker. Those shown in Group K are of interest because in silicates we usually have to deal with compounds in which no pairs of electrons are held in common between atoms. Thus in the octet equation $2p = 8n - e$ we place $p = 0$ and find $e = 8n$. In silicates, oxygen is the only element which forms octets, so n is equal to the number of oxygen atoms. This condition ($e = 8n$) is practically the only valence condition that needs to be fulfilled by silicates, and it is thus a complete statement of the valence theory for these compounds. The isomorphism of the two compounds of Group K is consistent with the octet theory since in both compounds the number of atoms is alike (13) and so is also the number of available electrons, $e = 8n = 64$.

SUMMARY

The octet theory of valence indicates that if compounds having the same number of atoms have also the same total number of electrons, the electrons may arrange themselves in the same manner. In this case the compounds or groups of atoms are said to be isosteric. Such compounds should show remarkable similarity in physical properties, that is, in those properties which do not involve a separation of the atoms in the molecule.

Table I gives a list of various isosteres predicted by the octet theory. For example, O^{--}; F^-; Ne, Na^+ and Mg^{++} are isosteric. Other examples are N_2—CO—CN^-; CH_4—NH_4^+; N_3^-—CNO^-; ClO_4^-—SO_4^{--}—PO_4^{---}; NO_3^-—CO_3^{--}, etc. In cases where isosteric groups have the same electric charges (isoelectric) their properties are directly comparable; thus N_2 and CO; N_2O and CO_2; KN_3 and KNCO, etc., are nearly alike (in pairs) in all their physical properties. But when the charges are unlike the similarity may manifest itself between properly chosen compounds; thus, according to the octet theory, we should expect sodium nitrate and calcium carbonate to have similar constitutions and therefore to have similar crystalline forms, as is in fact known to be the case.

The following cases of crystalline isomorphism are thus predicted by the theory and are found to exist according to published crystallographic data: NaF—MgO; KN_3—KNCO; KNO_3—$SrCO_3$; $KClO_4$—$SrSO_4$; $NaHSO_4$—$CaHPO_4$; $MnSeO_4.2H_2O$—$FeAsO_4.2H_2O$, etc. The following cases are predicted by the theory but cannot yet be tested because of lack of available data: MgF_2—Na_2O; K_2S—$CaCl_2$; $NaClO_3$—$CaSO_3$; $KHSO_3$—$SrHPO_3$; $Na_2S_2O_6$—$Ca_2P_2O_6$; $Na_2S_2O_7$—$Ca_2P_2O_7$; etc.

The theory of isosterism makes it possible to derive certain relationships in a very simple manner. Thus since argon is an isostere of the potassium ion and methane is an isostere of the ammonium ion, it follows that the potassium and ammonium ions must have similar properties because argon and methane are nearly alike in physical properties. Similarly, the relation between argon and nitrogen enables us to trace an equally close relationship between the cyanogen and the chlorine ions. From the similarity in the solubilities of nitrates and perchlorates we may also conclude that carbonates and sulfates should be closely related.

The experimental data discussed prove that the crystalline form of substances depends on the structure as given by the octet theory, thus indicating that this theory gives a true picture of the constitutions of crystalline solids. In particular, the experimental results justify the following conclusions:

1. The covalence of sodium, potassium, chlorine in chlorides, is zero.
2. The covalence of the central atom is 4 in nitrates, carbonates, sulfates, perchlorates, phosphates, permanganates, chromates, selenates, arsenates, borofluorides, etc.
3. Carbonates and sulfites are not isomorphous, the covalence of the central atom being 4 and 3, respectively.
4. Nitrates and chlorates are not isomorphous, the covalence of the chlorine being 3 in chlorates.
5. The applicability of the octet theory to complex inorganic compounds receives further confirmation by its ability to explain such cases of isomorphism as between Na_2BeF_4 and $MnCl_2.4H_2O$; K_2SO_4 and $ZnI_2.4NH_3$, $K_2SnCl_4.2H_2O$ and $K_2FeCl_5.H_2O$, $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$, etc.

Chapter Twelve

THE EFFECTS OF MOLECULAR DISSYMMETRY ON PROPERTIES OF MATTER

The kinetic theory of gases during the last century led to extremely valuable conceptions and even quantitative laws, notwithstanding the fact that in the development of the theory, it had been necessary to make many simplifying assumptions which frequently were not actually correct. For example in most derivations it was assumed that the molecules were infinitely hard elastic spheres which acted on one another only at the instant of contact. In this way it was possible to account quantitatively with fair accuracy not only for the effects of pressure and temperature on the volume, but for the viscosity, heat conductivity and diffusion of gases, and other phenomena involving the free paths of the molecules. Maxwell, on the other hand, developed a very complete theory based on the assumption that the molecules are point centers of force repelling one another according to the inverse fifth power of the distance between them. This assumption was made not because it was supposed to correspond to the actual forces around molecules, but because it lent itself particularly well to mathematical treatment. The results obtained by Maxwell differed from those based on the assumption of elastic spheres mainly in slight differences in numerical coefficients of the equations obtained. To handle the problem mathematically it was necessary to make assumptions as to the forces between the molecules, but to get most of the essential truths of the kinetic theory it did not much matter exactly what these assumptions were.

To account for the main features of the transition from the gaseous to the liquid state Van der Waals found it necessary to consider attractive forces, but again the particular law of force did not need to be known to obtain this useful result. Sutherland also took into account attractive forces in dealing with the temperature coefficient of the viscosity of gases.

In considering other properties of gases or liquids it may be necessary to analyze the forces around molecules in more detail. For example, Debye [1] showed that the variation of the dielectric constant of a substance with temperature depends on an orientation of the molecules in an electric field, thus indicating that these molecules are electric dipoles.

W. B. Hardy[2] in discussing the interfacial surface tension between fluids said in 1912:

"If the stray field of a molecule . . . be unsymmetrical, the surface layer of fluids and solids, which are close packed states of matter, must differ from the interior mass in the orientation of the axis of the fields with respect to the normal to the surface, and so form a skin on the surface of a pure substance having all the molecules oriented in the same way instead of purely in random ways."

In a later paper[3] he adds:

"The surface film must therefore have a characteristic molecular architecture. . . . When the composite surface is formed its architecture is determined by the interaction of the fields of force of molecules of A and B under the influence of the attraction of B for A."

In connection with a study of chemical reactions at the surfaces of highly heated tungsten and carbon filaments in gases at low pressures (less than 0.1 mm.) I came to the conclusion[4] that adsorbed carbon monoxide must be regarded as oriented on the surface, so that the carbon atoms are attached to the solid while the oxygen atoms form the surface layer.

Shortly thereafter, without at that time knowing of Hardy's work, I saw the application of these ideas to the orientation of molecules at the surfaces of liquids, and was then able to develop a theory of the effect of chemical constitution on the surface tension of pure liquids as well as solutions and oil films on water.*

It is the object of the present paper to consider in a general way the causes of molecular orientation and the effects produced by such orientation on surface tension, solubility, vapor pressure, etc. In particular, since the chemist knows a good deal about the shapes of molecules and the stray fields around their different parts, it will be urged that this knowledge be used to correlate, as nearly quantitatively as possible, the various so-called physical properties which depend on these factors. For this purpose it will not be necessary to have knowledge of the exact shapes and fields of forces of the molecules, but, just as in the case of the kinetic theory, considerable progress may be made even by the crudest kinds of assumptions in regard to these factors.

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* A paper on this work was read before the American Chemical Society in September, 1916, and a two-page abstract was published in *Met. Chem. Eng.*, *15*, 468 (1916). Before the full work could be published, two papers by W. D. Harkins appeared in *Jour. Amer. Chem. Soc.*, *39*, 354 and 541 (1917), which dealt in detail with the surface tensions of pure liquids. In the final publication of my results, *Jour. Amer. Chem. Soc.*, *39*, 1848 (1917), the part dealing with pure liquids was therefore omitted.

We know that molecules actually exist and must be of the most varied shapes. Let us therefore consider how the various possible shapes of the molecules and the types of force fields must influence the physical properties of substances.

TYPES OF INTERATOMIC AND INTERMOLECULAR FORCES

The chemical properties of matter are primarily dependent on the number of electrons in the atoms and the manner in which these electrons are able to arrange themselves to form the most stable configurations. The electric forces due to charges on the atoms frequently oppose the formation of certain configurations which, except for these charges, might be the most stable. The effect of these two factors in governing chemical action has been discussed at some length by the writer.†

The electron configurations existing in the atoms of the inert gases He, Ne, Ar, etc., are the most stable of all. Other atoms, by taking up, or giving up electrons, or by sharing electrons with each other, strive to obtain electron configurations like those of the inert gases. It is mainly as a result of these changes that chemical interaction occurs.

Each of the ions O^{--}, F^-, Na^+, and Mg^{++} contains 10 electrons, the same number as in a neon atom. The reason for the formation of chemical compounds containing these ions is that the electrons can thereby become arranged in the stable configuration characteristic of the neon atom.

This view, which is largely that of Lewis and Kossel, and is now generally accepted, may serve as a basis for a classification of intermolecular forces. There are three main types of molecules to consider: * (1) Non-polar, (2) Polar, and (3) Ionic, as follows:

1. Non-polar.

The neon atom, or methane molecule, may be taken as the most extreme example. The center of gravity of the electrons of the molecule coincides with that of the positive charges of the nuclei, so that there is no dipole moment. In general, however, the atom or molecule may behave as an electric quadrupole or system or even higher symmetry. Debye has shown that quadrupole molecules † attract one another, when at a considerable distance, with a force which varies inversely with the ninth power of the distances. This result is obtained by considering the deformation of each of two molecules in the electric field of the other. Under the influence of an electric field the electrons become displaced with respect to the nucleus by an amount which may be estimated from the dielectric constant, and thus the molecule becomes polar to a degree which depends on the proximity of other molecules. If the molecule is more symmetrical than a quadrupole (as neon probably is), the force will vary inversely with a power of the distance which may be much greater than the 9th.

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† "Types of Valence," I. Langmuir, *Science, 54*, 59–67 (1921). The recent work of Bohr, which has proved that the electrons in the heavy atoms (such as nitron) are arranged in shells according to the scheme 2, 8, 18, 32, 18, 8 instead of the scheme 2, 8, 8, 18, 18, 32 postulated by the writer, requires only a slight and obvious modification of the wording of Postulate I, and does not otherwise affect the validity of the conclusions that were drawn in that paper.

* P. Debye, *Phys. Zeit., 21*, 178 (1920), has made this classification based on the degree of symmetry of the distribution of electrons within atoms.

† The word molecule will be taken to include atoms in those cases where the atoms act as individuals, as, for example, in gaseous or liquid neon.

In general, non-polar molecules do not become oriented in weak electric fields, but when the field becomes very strong, the dipole moment, which may differ for different orientations of the molecule, may cause orientation. However, thermal agitation will nearly always make such orientation negligible for molecules of this type.

2. Polar.

The molecules of hydrochloric acid gas and water vapor are extreme examples. The center of gravity of all the electrons of the molecule does not coincide with that of the positive charges, so that the molecule acts as an electric dipole. If the separation of the centers of gravity of the electric charges is comparable with the distance between the atoms in a molecule the electric forces are much more intense than in the case of non-polar molecules. The attractive force due to deformation is thus greater than for non-polar molecules. The polar molecules become oriented in an electric field in so far as the thermal agitation will permit. Thus the dielectric constant, or rather that part of it which is due to orientation, varies inversely proportional to the absolute temperature.[5] Such orientation of the polar molecules in the field of neighboring molecules, if it occurs to any large degree, causes a very great increase in attractive force between molecules. The amount of orientation increases rapidly as the molecules are brought closer together, and also increases slowly as the temperature is lowered. The force of attraction between two dipole molecules which are oriented in each other's fields is $6e^2\delta^2/r^4$ where e is the charge and δ the displacement of the dipole ($e\delta$ = the electric moment) and r is the distance between the the molecules. The force due to orientation thus varies inversely with the fourth power of the distance.

3. Ionic.

Electrolytic ions such as Na^+, SO_4^{--}, etc., are familiar examples. Gaseous ions must also be included in this group. The molecule, which in this case is an ion, has an unequal number of electrons and protons, or, in other words, the number of electrons is not equal to the positive charges of the nuclei. The electric field around such ions is in general very much greater than around polar and non-polar molecules, and falls off still more slowly as the distance increases. The force between two ions in free space varies inversely as the square of the distance between the ions. But in presence of other molecules, and particularly in presence of other ions, the deformation of the non-polar molecules, the orientation of the polar molecules, and the concentration differences among the ions all tend to decrease the forces between ions. The increased concentration of positive ions around negative ions and vice versa causes the force between two given ions to decrease with increasing distance more rapidly than according to the inverse square law. Debye and Hückel [6] have recently been able to develop a mathematical theory of these effects which has cleared up at one stroke most of the perplexing problems involved in the theory of electrolytic dissociation.

Attractive Forces.

From this analysis we see that there are three fundamental factors that cause attractions between molecules:

a. Deformation
b. Orientation
c. Segregation

Debye has shown that two uncharged molecules, each consisting of a *rigid* structure of positive and negative particles, would on the average exert no force on one another if all orientations of the molecules are equally probable. But, since all substances have dielectric constants greater than unity, the particles must become deformed when they get into each other's fields. This deformation is always such as to cause an attraction between the molecules.

In general, there will also be a tendency for molecules to be oriented when they approach one another sufficiently closely. This orientation always increases the attractive force.

Debye has also pointed out that if, around a given ion in an electrolyte, there were no concentration of ions of opposite sign, there would be no resulting attraction between an ion and its neighbors. But since there is in fact around any ion an increased concentration of ions of opposite sign, there is a resulting attractive force which opposes the osmotic pressure of the ions, due to their thermal agitation. It is this effect which we have denoted by the term *Segregation*. It may occur not only with ions, but also with dipole molecules such as those of water. By the segregation of dipole molecules and their orientation about a given molecule or ion electric forces may be transmitted through distances larger than would otherwise be possible.

Repulsive Forces.

Of course the attractive forces in matter must be balanced by equal repulsive forces. Very little has been definitely known about these forces except that they vary inversely with some very high power of the distance between molecules. In the past in the kinetic theory it has been usual to take into account these repulsive forces merely by assuming that the molecules behave like infinitely hard elastic spheres which is equivalent to assuming that the force varies inversely with an infinite power of the distance.

In order to account for the compressibility of solids Born and Landé[7] have shown that definite exponents for the repulsive force must be assumed. Thus in the case of halide salts of the alkalis such as NaCl, KI, etc., he showed that the compressibility of the solid salts indicated that the repulsive force varied inversely as the 10th power of the distance between the ions, while the attractive force varied inversely as the square of the distance in accord with Coulomb's Law. Born[7a] also attempted to show that the inverse 10th power law for repulsion could be *deduced* by assuming that the electrons in the ions were arranged with cubic symmetry as at the corners of a cube. This attempt, however, must be regarded as a failure for two reasons. 1st. The method of mathematical expansion used is not legitimate when applied to distances as short as those between ions in salts, and 2nd, Born assumed that the cubical ions were all oriented so that their edges are parallel. This kind of orientation would be unstable under the forces assumed. If the atoms should become oriented in response to the forces acting, the repulsive force would disappear and would be replaced by an attractive force which would act in addition to the force between the ionic charges.

Such orientation of ions as Born assumes may very possibly exist in solid crystals from causes which he does not discuss, but this orientation cannot be the cause of the repulsive forces which determine the compressibility, since the elimination of the orientation by melting the salt does not greatly alter the density or the compressibility, whereas by the reasoning of Born's theory the repulsive forces, being then unbalanced, should cause a complete collapse of the structure.

Thus we cannot regard Born's theory as one that throws any light on the cause of the repulsive forces.

Debye,[8] however, has recently developed a theory which seems to indicate the nature of the repulsive forces. It depends essentially on the orbital motions of the electrons within the atoms in accord with Bohr's theory, whereas Born in his calculations had assumed that the electrons acted as if stationary. Debye assumes that the conditions imposed by the quantum theory determine the size of the electron orbits and the frequency of rotation in these orbits. Thus the electric field around an atom or molecule is not a static field but is a pulsating or partly oscillating field increasing in amplitude of oscillation very rapidly as the surface of the atom is approached. Thus when an electron approaches an atom it acquires in addition to any motion of translation it may have, an oscillatory motion due to the pulsating field. Debye shows that this oscillatory motion tends to be 180° out of phase with the field producing it, and then shows, that because of the non-uniformity of the electric field near an atom, the resulting force will be one of repulsion. This repulsive force may be assumed to exist not only for free electrons but for electrons which themselves are involved in the orbital motions of other atoms.

Thus the repulsive forces between atoms and molecules are due to the perturbations in the electron orbits caused by the motions of the electrons which revolve in orbits in neighboring atoms. The repulsive force does not originate from an atom as a whole, but comes from the close approach of electrons in the two atoms. Thus we should look upon these forces as surface forces and should try to express them as functions of the distances between the surfaces of the atoms (fixed by the outer electron orbits) rather than in terms of the distances between the centers of the atoms.

FORCES AT THE SURFACES OF MOLECULES

In a discussion of the compressibility of metals and its relation to interatomic forces [9] the writer has shown that the range of the attractive forces between the atoms is approximately the same for all metals, although the compressibilities of the metal and the volumes of the atoms vary over wide ranges. Thus although the compressibility of cæsium is 220 times that of tungsten, and the atomic volume is 7.4 times that of tungsten, the range of the attractive force is nearly the same, 0.66×10^{-8} and 0.57×10^{-8} cm. respectively.

Debye [10] in a paper of 1920 in analyzing the causes of attractive forces between non-polar molecules attempts to calculate the force from assumed stationary electron configurations. For this purpose he expressed the electric potential in the neighborhood of a given molecule in terms of an infinite series expanded according to reciprocal powers of the distance r from the center of the molecule. If the molecule is uncharged (*i.e.,* is not ionic) the first term which involves $1/r$ vanishes. If the molecule is non-polar (*i.e.,* has no electric dipole moment) the second term involving $1/r^2$ vanishes. For a non-polar molecule, which is of the type of a quadrupole, the third term is therefore the first term which does not vanish. Debye considers therefore the effects due to this term involving $1/r^3$ and *neglects all subsequent terms in the series.* If, however, the molecule has a higher degree of symmetry than that of a quadrupole (for example a tetrahedron or cube) the third term (which is the only one that Debye considers) should also vanish.

Debye then calculates that the average force which acts on a molecule B when at a distance r from a similar molecule A is given by

$$F = \frac{24\alpha\tau^2}{r^9} \tag{1}$$

where r is a function only of the "electric moments of inertia" (Σex^2, Σey^2 and Σez^2) determined by the positions of the electrons and nuclei in the molecule. The quantity α measures the deformability or ease of polarization of the molecule in an electric field and can be calculated from the dielectric constant, or better from the molecular refractive index.

Debye then proceeds to test these conclusions by calculating from this equation the coefficient a in the van der Waals' equation.

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \tag{2}$$

which measures the attractive forces between molecules. He finds

$$a = \frac{6\pi}{5} \frac{N^2\alpha\tau^2}{d^5} \tag{3}$$

where N is the Avogadro constant (6.06×10^{23}) and d is the diameter of the molecule. In deriving this relation Debye assumes that the force between the molecules is given by Equation 1 for all distances from d to ∞. Considering the derivation of Equation (1) it is clear that we have no right to apply it to distances comparable with the diameter of the molecule, for the neglected terms in the expansion on which it is based, should then be as important as the term actually considered. Debye, however, uses Equation 3 to calculate τ from the experimentally determined values of a.

He then compares the values of τ obtained in this way with those calculated by another method from the Sutherland constant c which is determined from the temperature coefficient of the viscosity η of gases by the equation

$$\eta = \frac{\text{const}\sqrt{T}}{1 + \frac{C}{T}}$$

The Sutherland constant is a measure of the attractive forces between molecules and thus Debye is able to express it in terms of τ which occurs in Equation 1.

The values of τ calculated by these two independent methods agree very well with one another (average error about 4 per cent) for the gases argon, krypton, xenon, nitrogen, oxygen and ethylene which have molecules of the non-polar type. For hydrogen and helium, however, the errors are about 50 per cent. Debye concludes that this good agreement indicates that "the law of force (Equation 1) and its interpretation correspond completely to reality." Undoubtedly the agreement justifies the use of the inverse 9th power law of attractive force between non-polar molecules and the relation between the attractive forces and the refractive index, but it should not be concluded that this is evidence of the correctness of the relation between τ and the assumed arrangement of electrons (electric moment of inertia).

With a force which varies with the inverse 9th power, the force falls to one-half value for an increase of only 8 per cent in the distance. Thus the cohesive forces corresponding to the van der Waals and Sutherland constants are determined mostly by the forces exerted by the molecules upon one another during the times that their distance apart does not exceed the distance of minimum approach by more than 10 per cent.

When a molecule is as close as this to another the force acting at the near side of the first molecule would be about 10000 times as great as the further side of the molecule. We are then surely not justified in considering that the deformation would be the same as if the molecule were in a uniform field having the intensity of that at the center of the molecule. The fact that Debye does get good agreement must be due to two compensating errors. 1st the field at the near side of the molecule where it alone needs to be considered is much stronger than that calculated by Debye, and 2nd this field acts effectively on only a small part of the molecule and its effect is thus reduced.

Examining Debye's data we find that the values of τ which he finds are quite accurately proportional to the 4th power of the molecular diameter. From this it can be shown that the root-mean square electric field at the surface of the molecule which causes the mutual polarization of the molecules when they are in contact is practically the same for all the substances considered, and has the value of 9.8×10^8 volts per cm. (for $r = d$) which is the field that exists at a distance 1.21×10^{-8} cm. from an electron.

Thus we see that the intensities of the fields around different non-polar molecules are practically identical when regarded as surface forces rather than as forces which originate at the center of the molecules.

SURFACE FORCES AS THE CAUSE OF MOLECULAR ORIENTATION

The surface tension γ of a liquid is the free energy per unit area or is that part of the surface energy which can do work. The total energy per unit area γ_0 is given by

$$\gamma_0 = \gamma - T \frac{d\gamma}{dT} \qquad (4)$$

To produce isothermally a new surface of unit area we must expend the work γ, but the total energy increases by more than this, the difference $-T\frac{d\gamma}{dT}$ being derived from heat energy, and thus causing a cooling effect. In general the temperature coefficient $\frac{d\gamma}{dT}$ is practically constant, and therefore by Eq. (4) γ_0 is constant and equal to the value of γ at $T = O$. From the linear change of γ with temperature it is probable that the variation of γ is a direct result of the thermal agitation of the molecules, and is not due to any change in the structure of the surface. In studying the effects of molecular orientation we must, therefore, consider the total energy γ_0 rather than the free energy.

In the early work on the orientation of the molecules in the surfaces of organic liquids, the writer pointed out that the different portions of the molecules produced their characteristic effects independently of the presence of the other portions of the molecular surface. Thus it was stated:[11]

> The surface energy of a liquid is not a property of the molecules, but depends only on the *least active portions of the molecules* and on the manner in which these are able to arrange themselves in the surface layer. In liquid hydrocarbons of the paraffin series the molecules arrange themselves so that the methyl groups at the ends of the hydrocarbon chains form the surface layer. The surface layer is thus the same no matter how long the chain may be. As a matter of fact the surface energies of the hydrocarbons from hexane to molten paraffin, have substantially the same surface energy (46–48 ergs per cm.^{2}) although the molecular weights differ very greatly. If we consider the alcohols such as CH_3OH, C_2H_5OH, etc., we find that their *surface energies are practically identical with those of the hydrocarbons.* The reason for this is that the surface layer in both cases consists of CH_3 groups.

We see that this conception of surface forces is in agreement with the conclusions that we have reached by our more general considerations of intermolecular forces. We may, however, use this idea of separate surface energies for different parts of the molecular surface, to explain the orientation of the molecules and many other phenomena observed in liquids.

Let us apply the idea of surface energy to the surface of a molecule in the same manner as we apply it to a large surface of a liquid. As an example we will consider a molecule of palmitic acid, $C_{15}H_{31}COOH$ and calculate the difference in surface energy when the molecule is in various environments. From the density 0.85 and the molecular weight 256 the volume per gram molecule is 301 cm^3 and from the Avogadro number we find the volume per molecule to be 497×10^{-24}cm^3. Because of surface tension forces a molecule of palmitic acid vapor will assume a nearly spherical form in which the carboxyl group is buried as completely as possible within the sphere. Thermal agitation and internal stresses in the molecule will tend to prevent the molecule from being truly spherical, but with a molecule as large as palmitic acid the effect of the surface energy should predominate and make the molecule approximately spherical. Let us estimate the maximum and minimum surfaces which the molecule may possess.

The minimum surface will correspond to the spherical form. The diameter of a sphere having a volume * of 497 A^3 is 9.83 A and its surface is 304. A^2. The maximum area occurs when the hydrocarbon chain is as nearly straight as possible. The experiments on adsorbed films on water have shown a minimum cross-section of 20 A^2 for the hydrocarbon chain. If we consider the molecule to be a cylinder having this cross-section and having hemispherical ends, we find the diameter to be 5.04 A, the length of the cylindrical part 21.5 A and the total surface 420. A^2, which is 39 per cent greater than the surface when the molecule is spherical.

The difference in surface (116. A^2) multiplied by the surface energy of hydrocarbons (50 ergs per cm.^2) gives the energy involved in the transformation between the cylindrical and the spherical form.

Let us then consider whether this energy of 58×10^{-14} erg is sufficient to cause the molecule to assume a nearly spherical form.

The ratio P_1/P_2 of the probabilities of the occurrence of any particular configuration of a molecule is given by the modified Boltzman equation

$$\frac{P_1}{P_2} = \frac{p_1}{p_2} e^{-\frac{\lambda}{KT}} \tag{5}$$

where λ is the energy required to change the molecule from the state 2 to state 1, and p_1 and p_2 are the *a priori* probabilities of the two states, which are largely determined by geometric factors and the definitions of the two states. If we put $\lambda = 58 \times 10^{-14}$, $T = 293$, the exponent is -14.4 and the exponential factor is thus 6×10^{-7} so that nearly all the molecules must be in a nearly spherical form unless p_1/p_2 has a very large value. If the surface energy λ were zero the ratio p_1/p_2 would measure the relative probabilities of the two configurations. Of course the probability p_2 would be zero if we were to consider only absolutely spherical molecules. We should therefore consider a range for each state, taking, for example, state 2 to be one in which the surface area is not more than 5 per cent greater than that of a perfect sphere, while state 1 is one in which the area is not less than 95 per cent of that of the cylindrical molecule already considered.

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* For convenience we shall express molecular dimensions in terms of the Ångstrom unit 10^{-8} cm.; thus $5\ A^2 = 5 \times 10^{-16}\ \text{cm.}^3$ and $4\ A^3 = 4 \times 10^{-24}\ \text{cm.}^3$ [A stands for Å.U. J. A.]

If λ were zero, thermal agitation would make the molecules assume the most varied shapes. It seems likely, however, that in most of these configurations there will be a relatively large part of the surface of the hydrocarbon chain exposed, so that p_1 will be larger than p_2. But this difference in probabilities will be a very moderate one, not at all able to compensate for the very small value of the exponential factor in Equation (5) when λ has the value $58. \times 10^{-14}$ erg.

In these calculations we have used the total surface energy γ_0 instead of the free energy. The thermal agitation may tend to oppose the contraction of the surface of a single molecule, but probably to a much smaller extent than in the case of a large surface of many molecules. However, the conclusion that there is ample energy to bring about a nearly spherical form would not be altered if λ were half as great as we found, so that for the present we shall not attempt to draw a distinction between free energy and total energy in applying Equation (5).

If a palmitic acid molecule is surrounded by water, the hydroxyl group is nearly completely surrounded by water molecules, while the hydrocarbon chain will draw itself as nearly as possible into a sphere, since the interfacial surface energy between water and hydrocarbon is about 59 ergs, which is even more than the surface energy of a hydrocarbon (against vapor).

Before proceeding with the properties of the palmitic acid molecule let us consider the somewhat simpler problem of a hydrocarbon molecule. To facilitate comparison we will assume that the hydrocarbon molecule has the same volume ($497A^3$) as the palmitic acid molecule. This corresponds approximately to hexadecane $C_{16}H_{34}$. Let us now calculate the energy needed to transfer such a molecule from a hydrocarbon liquid to —1, the interior of a mass of water; 2. a vapor phase, and 3. an adsorbed film on the surface of the water.

While the hydrocarbon molecule is in a liquid consisting of other (saturated) hydrocarbons its surface energy may be taken to be zero, since there are no interfaces, even if the surrounding hydrocarbon molecules are of different molecular weight. When the molecule is transferred to the interior of a large volume of water the surface energy is $\lambda = s\gamma_0$ where s, the surface of the molecule, is 304 A^2 and the interfacial surface energy $\gamma_0 = 59$ ergs per cm. Hence $\lambda = 179 \times 10^{-14}$ erg. For the formation of a molecule of vapor we have the same value of s but $\gamma_0 = 50$ so that $\lambda = 152 \times 10^{-14}$.

These energies correspond respectively to the heat of solution and the heat of evaporation of the hydrocarbon molecule. Actually the heat of evaporation is about 55 per cent of the value calculated in this way. The agreement as to order of magnitude is satisfactory. The surface energy 50. ergs per cm^2 is that which is measured when a fraction (probably about ⅓) of the surface of the molecules is exposed, while the heat of evaporation corresponds to the whole surface exposed. It is probable that the difference is caused by the more unsymmetrical state of the molecule when only part of its surface is exposed and by the resulting increase in the surface energy or stray field.*

From the fact that λ for the hydrocarbon molecule in water or in the vapor state is so large we may conclude from the Boltzmann equation that the vapor state is so large we may conclude from the Boltzmann equation that the vapor pressure and the solubility are very small in the case of a hydrocarbon with a molecule as large as we are considering (16 carbon atoms). With lower molecular weights the surface area of the molecules becomes less and the volatility and solubility thus increase. The relatively small solubility of even the lower hydrocarbons may be explained in this way.

The energy of transfer of a hydrocarbon molecule to an adsorbed film on water will depend on the configuration and the orientation of the molecule in the surface. Let us consider three possible cases:

a. A spherical molecule half immersed in the water. The energy λ is thus the sum of the energies of the two hemispherical surfaces minus the energy of the water surface which is destroyed by the presence of the hydrocarbon molecule. The cross-section of the molecule through the center is 76.A^2 while each hemisphere has a surface of 152.A^2. Taking the total surface energy of water to be 117 ergs per cm.^{2} we have

$$\begin{aligned}\lambda &= (59 \times 152 + 50 \times 152 - 117 \times 76)\ 10^{-16} \\ &= 77\,.\times 10^{-14} \text{ ergs.}\end{aligned}$$

b. A cylindrical molecule, half immersed in the water, oriented with its axis parellel to the water surface. The area of the section parallel to the axis is 128.A^2 and half the molecular surface is 210 A^2 so that

$$\begin{aligned}\lambda &= (59 \times 210 + 50 \times 210 - 117 \times 128)\ 10^{-16} \\ &= 79\,.\times 10^{-14} \text{ erg.}\end{aligned}$$

c. A cylindrical molecule, half immersed in the water, oriented with its axis perpendicular to the water surface. The cross-section of the molecule parellel to the water surface is 20.A^2. Thus we have

$$\begin{aligned}\lambda &= (59 \times 210 + 50 \times 210 - 117 \times 20)\ 10^{-16} \\ &= 206. \times 10^{-14}\end{aligned}$$

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* In a paper to be published in the *Journal of Physical Chemistry* this theory of evaporation is developed and discussed in more detail and gives quantitative agreement with the heats of evaporation not only of hydrocarbons, but of alcohols and other substances.

Table I gives a summary of these results to facilitate comparison.

TABLE I

SURFACE ENERGY OF A HYDROCARBON MOLECULE $C_{16}H_{34}$ HAVING A VOLUME 497. A^3

Sphere 9.83 A diameter or Cylinder 5.04 A diameter
304. A^2 surface 420. A^2 surface

Location of Molecule	Shape and Orientation of Molecule	Energy in Erg $\times 10^{-14}$
In liquid hydrocarbon	Sphere or Cylinder	0
In water	Sphere Cylinder	179. 248.
In vapor	Sphere Cylinder	152. 210.
Adsorbed on water (half immersed)	Sphere Horizontal cylinder Vertical cylinder	77. 79. 206.

Surface energies used in calculations—water vs. vapor 117, water vs. hydrocarbon 59; hydrocarbon vs. vapor 50 ergs per cm. as taken from tables by Harkins et al.

The difference in energy between the spherical and cylindrical form when the molecule is in the vapor phase or the water phase is so great that the molecules will be nearly spherical. But with the molecule in the interface the difference in energy (2×10^{-14}) between the sphere and the horizontal cylinder is so small that it will have little effect in determining the shape, the exponential factor in Equation 5 being only 0.61. Thus the configuration of the molecule will depend almost wholly on the *a priori* probabilities. For reasons already given a nearly spherical form is improbable as compared to an extended or irregular form in which the larger part of the molecule is exposed. These considerations lead us to conclude that a hydrocarbon molecule adsorbed on a water surface will lie flat on the surface when not crowded by other absorbed molecules.

This conclusion is the same as that reached by the writer from a study [12] of the surface tension of dilute solutions having non-saturated adsorbed films.

The very high value of λ in the case of the vertical cylinder shows that molecules can be oriented vertically only very rarely. The difference in energy between the horizontal and vertical cylinder (127×10^{-14}) gives, when substituted in Equation (5), an exponential factor of 2×10^{-14}. In this case the *a priori* probabilities of the two orientations are the same so that only one adsorbed molecule out of about 10^{14} will be oriented in a vertical direction.

The energy 79 corresponding to the adsorbed molecule is very much less than the 152 for the vapor or 179 for the water phase. We can thus see that the presence of molecules in the interface is very much more probable than in either the water phase or the vapor. This conclusion is strikingly in accord with the facts.

Hexane vapor coming into contact with water lowers its surface tension very considerably. According to Gibbs' Law this proves that there is an adsorbed film of hexane molecules in the surface having a much higher concentration than that of either the vapor phase or the water phase. With hexane the energy of transfer to the adsorbed film is roughly about $6/16$ths of that for hexadecane but the ratio of this energy to that in the vapor or water phase is about the same for the heavier molecule. As the length of the chain increases the vapor pressure, solubility and amount of substance adsorbed decrease, but the ratio of the amount adsorbed to that in either phase must increase.

We shall see that this is the fundamental cause of the formation of monomolecular films of organic substances on water. The *ratio* between the concentration of the substance in the film and in the water is not greatly altered by the presence of an active group (such as carboxyl) in the molecule. The principal effect of the active group is to increase the solubility of the substance in water and therefore cause a corresponding increase in the amount adsorbed.

The Effect of an Active Group.

When we replace a hydrogen atom in a hydrocarbon by a hydroxyl, carboxyl or similar radical we change the surface energy of a part of the molecule very greatly without having very much effect on the remainder of the molecular surface. From this viewpoint we have at once an explanation of the fact that the introduction of such a radical or active group lowers the vapor pressure and increases the solubility.

Let us now take up again the consideration of the palmitic acid molecule as an example of a molecule having an active group. We shall adopt Adam's terminology and refer to the hydrocarbon portion of the molecule as the tail and to the active group—COOH as the head. Representing the molecule by the usual symbol RX we shall thus let R denote the tail and X the head. For the calculations of the surface energies we shall adopt the following values for the surface energies (ergs per cm.^{2}).

$$\gamma_R = 50. \qquad \gamma_{RW} = 59.$$
$$\gamma_X = 144. \qquad \gamma_{RX} = 20.$$
$$\gamma_W = 117. \qquad \gamma_{XW} = -30.$$

The subscript w refers to water. The surface energies of hydrocarbons and of water, γ_R and γ_W respectively are the values we have already used and are those given by Harkins for the liquids in bulk. The same is true for the interfacial energy γ_{RW}. The value of γ_X has been obtained from a study of heats of evaporation of hydrocarbons and fatty acids while γ_{RX} and γ_{XW} were found from a study of the vapor pressures of binary mixtures by a method which we shall soon describe briefly. The negative value for the surface energy between carboxyl and water which results from these studies is in accord with the very marked increase in the solubility in water caused by the presence of this group.

We have already estimated the surface area of the palmitic acid molecule, but we now need to know the surface of the carboxyl group. From a comparison of the volumes of the molecules of the lower fatty acids we may estimate the surface to be 45.A^2 which is the value that was assumed in obtaining the values of γ_X, γ_{RX} and γ_{XW}.

Table II gives the dimensions of palmitic and butyric acid molecules

TABLE II

Dimensions of Palmitic and Butyric Acid Molecules

	Palmitic Acid $C_{15}H_{31}COOH$	Butyric Acid C_3H_7COOH
Molecular weight	256.	88.
Density	0.85	0.96
Volume per molecule	497. A^3	150. A^3
Sphere		
Diameter	9.83 A	6.59 A
Total surface	304. A^2	136. A^2
Surface of head	45. A^2	45. A^2
Surface of tail	259. A^2	91. A^2
Section of tail	76. A^2	34. A^2
Cylinder with Hemispherical Ends		
Diameter	5.04 A	5.04 A
Length of cylindrical part	21.50	2.80
Total surface	420. A^2	146. A^2
Surface of head	45. A^2	45. A^2
Surface of tail	375. A^2	101. A^2
Transverse section of tail	20. A^2	20. A^2
Longitudinal section of tail	108. A^2	34. A^2
Hexagonal Prism		
Side of hexagon	2.64 A	2.64 A
Total surface	420. A^2	146. A^2
Transverse section	20. A^2	20. A^2
Longitudinal section	108. A^2	34. A^2

calculated from the molecular volumes assuming three different shapes. The hydrocarbon tail is taken as spherical, cylindrical or of the form of a hexagonal prism, this latter shape being useful when considering molecules packed in surface films.

The surface energies of these molecules in various environments have been calculated from the data in Table II by means of the assumed values of the γ's and the results are given in Table III. The assumed locations and orientations are illustrated diagrammatically in Fig. 1, in which the numbers correspond to those in the first column in Table III. The relative lengths and diameters shown in Fig. 1 agree with those given for palmitic acid in Table II except that the molecule marked 6b illustrates the butyric acid molecule in a cylindrical form.

As an example of the method of calculating the surface energy let us consider Case 10 in which a molecule of palmitic acid is adsorbed on a water surface. The hemispherical upper end of the molecule which extends above the water has a surface of $40.\text{A}^2$ and since the surface energy γ_R is 50 this part of the molecule contributes $20. \times 10^{-14}$ erg. The surface of the chain in contact with the water is $375 - 40 = 335$, and the surface of the head is 45. The surface of water destroyed by the presence of the molecule is 20, so that the total energy, obtained by multiplying these surfaces by the corresponding γ and adding is $(40 \times 50) + (335 \times 59) + (45 \times -30) - (20 \times 117) = 181. \times 10^{-14}$ erg.

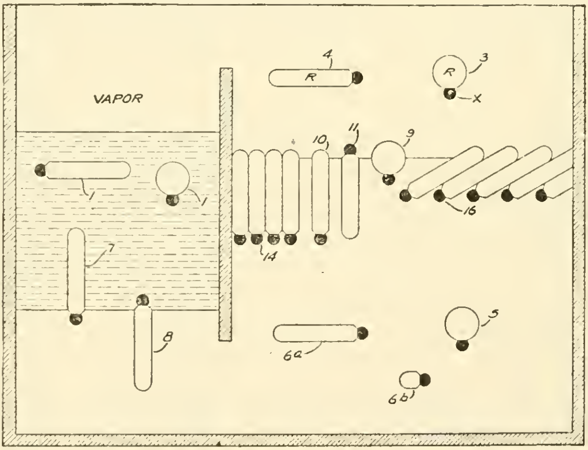

Fig. 1.—Diagram illustrating the various locations and environments of molecules considered in Table III.

In Case 2 where we consider a palmitic acid molecule in liquid palmitic acid we assume a random distribution of the molecules of the liquid. Each molecule has a tail having a surface of 375. while the surface of the head is 45, the head thus occupying 10.7 per cent of the whole surface. Considering the tail of a given molecule, we thus conclude that 0.107 of 375 or 40.2 is the area of the tail in contact with the heads of neighboring molecules

TABLE III

Surface Energies of Palmitic Acid and Butyric Acid Molecules in Various Environments. (See Fig. 1.)

Case No.	Location of Molecule	Shape and Orientation	Surface Energy Palmitic Acid — 10^{14} Erg	 Butyric Acid — 10^{14} Erg
1.	In liquid hydrocarbon	Sphere or Cylinder	9	9
2.	In its own liquid (palmitic or butyric)	Cylinder	8	6
3.	In vapor phase (head exposed)	Sphere	189	111
4.	" " " " "	Cylinder	252	115
5.	In water	Sphere	139	40
6.	" "	Cylinder	203	46
7.	At interface between water and hydrocarbon	Cylinder, vertical, X down	—37	—37
8.	At interface between water and hydrocarbon	Cylinder, vertical, X up	207	45
9.	Adsorbed on water surface (single molecules)	Sphere (half immersed)	39	—4
10.	Adsorbed on water surface (single molecules)	Cylinder, vertical, X down	181	19
11.	Adsorbed on water surface (single molecules)	Cylinder, vertical, X up	236	74
12.	Adsorbed on water surface (single molecules)	Prism, horizontal	64	1
13.	Adsorbed at edge of film	"	— 4	— 8
14.	" " " " "	" vertical	—17	—17
15.	" in single vacancy in film	" horizontal	—78	—32

while the remainder of the tail is in contact with other tails and therefore has no surface energy. Similarly we see that 0.107 of 45 or 4.8 is the area of the head in contact with other heads while the remaining 40.2 of surface is in contact with tails. Thus the surface energy $2 \times 40.2 \times 20 \times 10^{-16} = 16.1 \times 10^{-14}$ erg is associated with the molecule we are considering. Only half of this energy, however, can properly be attributed to this molecule for if these interfaces are destroyed by removing the molecule (leaving a cavity) half the energy in question (viz. $8. \times 10^{-14}$) can be recovered by allowing the cavity to collapse. Thus $8. \times 10^{-14}$ erg represents the surface energy of a palmitic acid molecule when surrounded by similar molecules.

Case 14 deals with a molecule oriented vertically at the edge of a surface film of similarly oriented molecules. The molecules are assumed to be hexagonal prisms arranged like the cells in honeycomb. On the average each new molecule added to the edge of the film makes contact with the molecules already present on three of the six faces of the prism. Three of the old faces are thus destroyed and three new ones are produced so that the lateral area of the edge of the film (whether in contact with vapor or water) is not altered by the presence of a new molecule. The change in surface energy due to the new molecule is thus:

1. The energy of the upper end in contact with vapor. This area may be estimated as $30 \times A^2$ so that the energy is $30 \times 50 = 15 \times 10^{-14}$.
2. The energy of the head in contact with the water. We may assume that the area $30.A^2$ is in contact with the water while the remaining $15.A^2$ of the head is in contact with the adjacent heads. This energy is thus $30 \times -30 = -9. \times 10^{-14}$.
3. The energy due to the water surface destroyed which is $-20 \times 117 = -23.4 \times 10^{-14}$.

The total energy of a palmitic acid molecule at the edge of a film is thus $15 - 9 - 23.4 = -17.4 \times 10^{-14}$ erg.

In Case 13 the new molecule at the edge of the film is assumed to lie horizontally being in contact with the other molecules of the film only over one of its six faces.

Case 15 deals with the change in energy when a molecule is removed from a surface film of horizontally packed molecules (not at its edge) so as to leave a vacancy.

An examination of the surface energies λ of the molecules in various environments as given in Table III shows that they explain many of the properties of these substances. The small difference between λ in Cases 1 and 2, being less than the value of kT (4×10^{-14} erg at ordinary temperature), indicates that both palmitic and butyric acids should be miscible with hydrocarbons in all proportions.

It is of interest to note that the difference between λ for a molecule in a hydrocarbon and in its own liquid increases as the chain becomes shorter. An example of an effect of this kind, sufficient to lead to relative insolubility, is observed in the case of methyl alcohol which is miscible with hexane in all proportions only at temperatures above 43° C.

The solubility of palmitic acid in water is immeasurably small while butyric acid mixes with water in all proportions at temperatures above − 2.5° C. These facts are in general accord with the values of λ given under Case 5. Comparing these with the values for the corresponding hydrocarbons (Table I) we see that the introduction of the carboxyl group lowers the value of λ by 40 units. This accounts for the great increase in solubility.

Comparing Cases 5 and 6 we conclude that the tail of the palmitic acid molecule in water must assume a nearly spherical form while with the butyric acid molecule, thermal agitation will be able to cause the tail to spread out as a chain.

The most interesting applications of the data in Table III are in connection with the arrangements of molecules in surface films. Comparing Cases 2, 5, 7 and 8 we see that the decrease in energy corresponding to Case 7 is so great that practically no molecules could exist in either a water phase or a hydrocarbon phase until the interface becomes saturated with molecules which are all oriented with their heads in the water phase. The relative number of molecules having this orientation as compared to those having the reverse orientation (Case 8) is found from the Boltzmann equation to be as $10^{26}:1$ for palmitic acid and $10^9:1$ for butyric acid.

In a similar way we may estimate the probabilities of the various possible orientations of molecules adsorbed at the free surface of water. The high value of λ in Case 11 in which the molecule is oriented vertically with the carboxyl group uppermost shows that no molecules can be in this position.

Without such analysis as we are now making it might seem that single molecules of palmitic acid adsorbed on the surface of water would take up a verticle position as is illustrated in Case 10, the carboxyl group being downwards. In fact N. K. Adam as one result of work described in a series of valuable papers [13] concludes that "expanded films are two-dimensional gases" * in which there is considerable space vacant between the molecules and that in these films "the molecules are oriented perpendicular to the water surface." † An examination of Table III shows, however, that the value of λ corresponding to this orientation has the high value of 181, while for a molecule lying flat in the water surface (with the carboxyl group turned downward into the water at one end of the molecule) λ is only 64 (Case 12). A slightly lower energy ($\lambda = 39$) is calculated (Case 9) for spherical molecules half immersed in the water surface. But the *a priori* probability of the spherical form (particularly in case of butyric acid) is so much less than that of the spread-out form of a molecule which lies flat, that this latter form becomes the more probable.

This conclusion that the hydrocarbon chains of adsorbed molecules lie flat in a water surface was reached by the writer in 1917[14] from a study of Taube's and Szyszkowski's data on the surface tensions of dilute aqueous solutions of fatty acids and other aliphatic compounds. The energy change involved in the transfer of a $-CH_2$ group from the interior of the solution to the surface was found to be constant and equal to 625 calories per gram molecule or 4.3×10^{-14} erg per molecule.

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* See paper by G. Friedel, Colloid Chemistry, No. 372, pp. 102, Aug. 1926. Some of the structures he describes may be one or two dimensional solids. J. A.

† In a footnote in his last paper Adam rejects the suggestion that I had made to him that the molecules in expanded films tend to lie flat on the water surface becoming overlapped if sufficiently crowded. He says "There is the more probable alternative, however, that as soon as the molecules have separated, through expansion of the films, they sink in among the water molecules so as to satisfy the attractive forces of the chains. If this is so they will probably remain vertical. Nevertheless it must be remembered that the pressure in two dimensions in the surface is only about one sixth of that expected from the gas laws, and no satisfactory explanation of this fact is at present available." The analysis in the present paper shows that a sinking of the molecules does not satisfy the attractive forces, but that the hydrocarbon chains must be in contact with one another whenever possible, otherwise they must lie flat in the surface.

By Table III the difference between λ for palmitic and for butyric acids, due to the 12 CH_2 groups, is 63 for horizontal molecules on water, while for molecules in solution it is 162 for cylindrical and 99 for spherical molecules. Thus the energy of transfer from the interior to the surface is 8.3×10^{-14} for each CH_2 if the molecule in water is cylindrical and 2.8×10^{-14} if it is spherical. The value 4.3×10^{-14} found from the 1917 work lies between these values and is thus consistent with the results given in Table III.

In discussing the spreading of adsorbed films of the higher fatty acids on water and in comparing these films with those of the lower fatty acids, it was pointed out in the 1917 paper that the films produced by small concentrations of the lower acids behaved like two-dimensional gases obeying the gas law

$$Fa = kT. \qquad (6)$$

Here F is the spreading force (dynes per cm.) and a is the area (in cm.^{2}) per adsorbed molecule. It was found that

> "in the case of the higher fatty acids the films do not spread upon the surface in the way required by this equation. Thus with palmitic acid the force F falls to 0.2 dyne per cm. when $a = 23$ A^2 whereas by the equation the force should be 17.5 dynes per cm. for this value of a.
>
> "Any solid or liquid film must have a certain tendency to spread on the surface by giving off separate molecules which follow the gas laws. This tendency may be measured as a 'surface vapor pressure.' With palmitic acid and higher fatty acids this pressure is less than 0.1 dyne per cm. The smallness of this pressure for the higher fatty acids must be due to attractive forces between the molecules powerful enough to prevent their separation. These same forces tend to prevent the film from evaporating from the surface into the vapor phase and from going into solution in the water. There are thus intimate relationships between the lowering of surface tension produced by fatty acids and the vapor pressures and solubilities of these substances. These relationships will be discussed in more detail in another part of this paper."

It was intended to publish the work here referred to as Part III of the paper on the Constitution and Fundamental Properties of Solids and

Liquids, but war work which began at that time prevented the carrying out of this plan. The present paper, however, deals with this subject in the manner that was then contemplated.

It was also shown in the 1917 paper that a film of palmitic acid on water at 16° C. resists compression with a force greater than 1 dyne per cm. only when *a*, the area per molecule, is less than 21.A^2. But if the water is heated to 45° the film resists compression when *a* is 33.A^2 and a similar value of *a* is found at 16° if a very small amount of acid is added to the water. Thus adding acid or raising the temperature causes the film to expand if the applied compressional force is not over 10 or 20 dynes per cm. Adam has called such films "expanded films." He believes, as we have seen, that the molecules in these films are in the condition of a two-dimensional gas and that the molecules are oriented vertically. Let us see what light is thrown on these questions by the calculations of Table III.

A palmitic acid molecule at the edge of a film of vertically close-packed molecules has an energy $\lambda = -4$ if the molecule is horizontal (Case 13) and $\lambda = -17$ if the molecule is vertical (Case 14) like those in the rest of the film. Thus the vertical orientation is the more probable. An isolated molecule lying flat in the surface (Case 12) gives $\lambda = 64$. The difference 81 is so great that the conclusion may be drawn that practically no molecules will exist isolated in the surface layer but that they will all exist in clusters in which the molecules have their hydrocarbon chains in contact with each other. These values of λ thus explain the observed fact that the two-dimensional gas pressure is negligible for palmitic acid films.

With a lower fatty acid such as butyric acid, however, the difference in energy between an isolated molecule in the surface and one located at the edge of a film is only 18 units so that it is not surprising that with these lower fatty acids the molecules, at least in dilute solutions, do follow the laws of two-dimensional gases.

That isolated molecules of palmitic acid in a water surface cannot exist in appreciable numbers is thus proved by the data of Table III and by the experimental observation that for values of *a* greater than say 40A^2, the spreading force is immeasurably small. Thus Adam's view that the expanded films consist of molecules which are largely isolated cannot be correct. What is then the proper explanation of the expanded films?

In the 1917 paper in discussing the arrangement of molecules in adsorbed films on the surfaces of fatty acid solutions it was concluded (page 1888) that in dilute solutions "the hydrocarbon chain lies spread out flat on the surface of the water, but as the concentration of the solution increases, the molecules become more closely packed and when the surface becomes saturated, the molecules are all arranged with their hydrocarbon chains placed vertically." The transition between the two states was assumed to take place in the manner that was suggested (on page 1865) for the expanded film of oleic acid, viz., in the expanded film "the molecules are partly reclining on the surface, while in the second case (compressed film) they are packed tightly side by side and are more or less erect upon the surface."

The area covered by a vertically placed palmitic acid molecule is about 20. A^2 while the same molecule lying flat on the surface should cover an area of about 108.A^2 (see Table II). Clearly then the expanded film occupying an area of at most 40 A^2 must consist of molecules which are only slightly inclined from the vertical. As a matter of fact there is no reason at all why the flexible hydrocarbon chains should orient themselves at any particular angle. They will be quite free to respond to thermal agitation and arrange themselves nearly in the same random manner as in a liquid hydrocarbon, the only restriction upon their motion being imposed by the condition that the *lower end* of each molecule must remain in contact with the underlying water. We can thus readily see why the expanded films are *always liquid* while the contracted or fully compressed films of vertically oriented molecules are frequently *solid*. Taking the volume of the hydrocarbon chain in the palmitic acid molecule as $450A^3$ (Table II) we see that the thickness of the hydrocarbon layer (in A units) will be $450 \div a$ where a is the area of the film per molecule (in A^2 units). Thus when $a = 20A^2$ the thickness is 22.5A while for an expanded film for which $a = 33A^2$ the thickness is 13.6A. Such an expanded film is represented diagrammatically by 16 in Fig. 1, the area per molecule corresponding to the inclination shown being about $a = 60.A^2$.

Consider an expanded film as covering a definite area of a water surface. If additional palmitic acid molecules are introduced into the film there is no change in the area of the free hydrocarbon surface. The energy of transfer of a molecule from any given location to an expanded film is thus the same as the energy of transfer of the molecule to an interface between hydrocarbon and water as illustrated by Case 7 in Table III and Fig. 1. According to the data of Table III the value of λ for a molecule of palmitic acid at the edge of a condensed film is -17 (Case 14) while for a molecule in an expanded film (Case 7) λ is -37. This would indicate that the expanded film should form in preference to the condensed film. However, the difference of 20 in the values of λ is not greater than the probable error so that the sign of the difference is somewhat uncertain. In considering the stability of expanded films we must take into account the applied compressive force and the effect of the forces acting between the heads of the molecules which are located in the interface between the hydrocarbon film and the water. To understand these relationships better let us analyze the problem as follows.

Let n molecules of a substance (which spreads on water) be present per unit area as an expanded film on the surface of water. The flexible hydrocarbon tails of the molecules are subject to little or no constraint except that due to the fact that they are attached to the heads which are constrained to remain in contact with the water. This constraint may well influence the degree to which the thermal energy of agitation of the hydrocarbon tails aids in spreading the film and may thus alter the relation between the total energy and the free energy which should be used in connection with the Boltzmann equation. But as a first approximation we may ignore such an effect of the thermal agitation, especially as we are willing to regard the surface energies γ_R, etc., as empirical quantities.

The expanded film may thus be looked upon as a layer of hydrocarbon liquid having at its upper surface a surface energy γ_R and having adsorbed in its interface with the water n active groups, or heads per unit area. Consider now that by means of a *two-dimensional piston* (for example a paper strip on the surface) the expanded film is allowed to cover only a part of the surface of the water. The spreading force F (in dynes per cm.) exerted by the film is measured by the mechanical force applied to the piston. On one side of the piston is a surface of water which exerts a force γ_W tending to cause the film to expand and on the other side is the expanded film whose *upper surface* exerts a force γ_R while the *lower surface* exerts a force which we may represent by γ_L. Thus for equilibrium we have

$$\gamma_W - F = \gamma_R + \gamma_L. \qquad (7)$$

If the molecules in the film did not have any active groups, the surface tension γ_L would be equal to the normal interfacial energy γ_{RW}. But the *active groups in the interface* because of their thermal agitation will tend to act like a two-dimensional gas. When these active groups or heads are far enough apart they will exert a force F_L following the gas law

$$F_L = nkT. \qquad (8)$$

When the molecules are packed as closely as in the ordinary expanded film, we should, by the analogy with the b term in the van der Waals equation, write

$$F_L(a - a_0) = kT \qquad (9)$$

where a_0 is the area per molecule for a highly compressed film.

Furthermore, the analogy with the equation of state for gases would suggest that when the film is compressed sufficiently, attractive forces between the active groups would come into play and that these might be largely responsible for the small spreading forces observed with some contracted films. In any case, however, we may place

$$\gamma_L = \gamma_{RW} - \mathrm{F}_L \qquad (10)$$

and thus from Equation 7 we get

$$F = \gamma_W - \gamma_R - \gamma_{RW} + F_L. \qquad (11)$$

For very low compressive forces we may neglect the attractive forces between the heads and thus by combining Equations (11) and (9) we get

$$(F - F_0)\ (a - a_0) = kT \qquad (12)$$

as our equation of state for expanded films. Here F_0 is used as an abbreviation for the three γ terms in (11) so that

$$F_0 = \gamma_W - \gamma_R - \gamma_{RW}. \qquad (13)$$

Thus we see that we should not expect the simple gas law of Equation 6 to hold for expanded films, but such a law should hold only after constants F_0 and a_0 have been subtracted from the observed values of F and a.

Examination of the experimental data on expanded films in my 1917 paper, and in Adam's papers, shows that the agreement with Equation (12) is very satisfactory. For large compressive forces deviations occur which are of the kind that are to be expected as a result of attractive forces between the heads of the molecules.* For example, Adam's curve (in this 3rd paper) for a film of myristic acid on water at 32.5° C. gives the equation

$$(F + 13)\ (a - 18) = kT$$

The value of a_0 is thus 18.A^2 while F_0 has the value -13 dynes per cm.

Let us compare this value of F_0 with that calculated by Equation (13). For water at 32.5° the free energy (surface tension) γ_W is 71.0 dynes per cm. The interfacial free surface energy γ_{RW} of octane is 50.4. Since the temperature coefficient is very low the total interfacial energy is about the same as the free energy. Our theory of the structure of the interface leads to the conclusion that the *total energy* is independent of the length of the hydrocarbon chain and since in this case the free energy and total energies are nearly the same the free energy will also be independent of the chain length. Thus for tetradecane (the hydrocarbon corresponding to myristic acid) we may put $\gamma_{RW} = 50.4$.

The free surface energy of octane at 32.5° is 20.4 and the total energy is 48.4. For tetradecane the theory indicates that the total energy will also be 48.4. The free surface energy is a linear function of temperature and becomes zero at the critical temperature. Taking the critical temperature of tetradecane as 680° K. we can thus estimate that the free surface energy at 32.5° C. should be 26.8.

These values for the γ's give $F_0 = +0.2$ for octane and $F_0 = -6.2$

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* See 3rd Colloid Symposium Monograph (Chemical Catalog Co., 1925).

dynes per cm. for hexadecane. This latter value does not differ greatly from that calculated from Adam's data on the myristic acid films ($F_0 = -13$). The difference is not greater than should be expected because of the uncertain part played by thermal agitation in the spreading of surfaces.

According to Equation (12) with negative values of F_0, the expanded film should not expand indefinitely even if the compressive force F is made negligibly small. Placing $F = 0$ we see that the maximum area covered per molecule will be

$$a_M = a_0 - \frac{kT}{F_0}. \tag{14}$$

For the case we have considered where $a_0 = 18$ and $F_0 = -13$, we obtain $a_M = 18 + 32.3 = 50.3A^2$ as the maximum area for an "expanded film" of myristic acid on water. This equation shows that the maximum area a_M depends principally upon F_0. By Equation (13) we see that F_0 is the difference between two relatively large quantities which are nearly equal. A very small percentage change in γ_R causes a relatively large change in F_0 and therefore in a_M. As a matter of fact Adam finds that a_M varies only moderately for different substances. As the length of the chain increases he finds a slight decrease in a_M and considers this a strong argument against the view that the molecules tend to lie flat if they have sufficient room to do so. We have seen, however, by our comparison of octane with tetradecane that γ_R and therefore $-F_0$ increases with the length of the chain, and therefore by Equation (14) a_M should actually increase as the chain is made shorter. The changes in a_M observed by Adam may be accounted for by very small percentage changes in γ.

Another factor which may need to be taken into account is that the value of γ_R for the CH_3 groups at the ends of hydrocarbon chains (particularly noticeable in iso-compounds) is about 10 per cent lower than for the CH_2 groups constituting the central portions of the chains. Thus as a film becomes more expanded the value of γ_R increases, tending to make the equilibrium of such a film more stable. Of course an expanded film can be dealt with by equations of the type we are now considering only as long as the upper surface forms a continuous hydrocarbon surface. The area of such a film is thus limited to that given by the molecules when they lie flat in the surface.

This theory of "expanded films" requires that the molecules remain in contact while Adam concluded that in such films the "molecules become separated and move about independently on the surface" and that "there are spaces not covered by molecules." Adam considered that the molecules of the film behave as a two-dimensional gas while we conclude that it is only the heads of the molecules that behave in this way.

It is hoped that the illustrations given in this paper have helped to prove the usefulness of the conception of separate surface energies for each of the different parts of complex molecules. It is believed that this viewpoint is applicable to the study of nearly all the physical properties of organic compounds, particularly to the calculation of the vapor pressures, solubilities, viscosities, and surface tensions of liquids and their mixtures.

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Chapter Thirteen

METASTABLE ATOMS AND ELECTRONS PRODUCED BY RESONANCE RADIATION IN NEON

In studies of arcs in pure neon at a few millimeters pressure, we have observed some phenomena which indicate that the resonance radiation from the arc can travel through the un-ionized neon beyond the end of the arc for distances of 20 to 30 centimeters, or more, and the absorption of this radiation produces, by excitation of the gas and by subsequent collisions of the second kind, metastable atoms at the rate of at least 10^{13} cm^{-3} sec^{-1}. In these experiments the neon arc carrying currents of approximately one ampere was passed through a long tube between a hot cathode at one end of the tube and an anode placed near the center. One or more collecting electrodes were placed in the tube beyond the end of the arc, and, in some experiments, movable collectors were used whose distance from the end of the arc could be varied.

The metastable atoms thus produced beyond the end of the arc diffuse into contact with the walls or with metallic electrodes and liberate electrons from the glass or metal surfaces which have velocities of the order of 5 to 10 volts. The walls thus become positively charged and within the space there is a definite concentration of electrons. If a collector is maintained at, say, 70 volts negative with respect to the anode, the electrons emitted by it serve as a measure of the concentration of the metastable atoms. The concentration of metastable atoms diffusing out of the arc should fall to $1/e^{th}$ of its value every time the distance is increased by an amount equal to 0.4 of the radius of the tube. Within a few centimeters of the end of the arc this theoretical decrement is actually observed, but at greater distances the concentration of metastable atoms decreases far more slowly.

The width of the line corresponding to the resonance radiation in the arc is far greater than that of the absorption line in the unexcited neon, which is determined mainly by the Doppler effect. Assuming this cause of broadening of the absorption line, it can be calculated that between parallel planes the energy absorbed per unit volume in the gas is inversely proportional to the distance from the source and thus, as the end of the arc is approximately a point source of this radiation, the rate of production of metastable atoms should vary approximately inversely as the cube of the distance from the end of the arc. The observed values are in accord with this theory.

The electrons in the tube generated at the walls by the metastable atoms give to the neon a conductivity whose value can be measured, and from the known mobility of the electrons in neon gas, the concentration of electrons can be calculated. For low voltages on the collectors, the currents are determined solely by this mobility of the electrons, and the volt ampere characteristics for small currents are thus linear on both sides of the zero point. For larger negative voltages, the current becomes limited by the number of electrons that can escape from the collector. For sufficient positive voltages, the currents increase more rapidly than corresponds to the linear relationships, this being due to ions produced within the tube by the acceleration of the electrons. The experiments prove that these ions are produced by the ionization of metastable atoms rather than normal atoms, for the rate of production of ions varies approximately with the square of the light intensity. These conclusions are confirmed by experiments with a shutter placed beyond the end of the arc, which can cut off the radiation without interfering with the diffusion of atoms, ions, etc., past the shutter. It is thus proved that the production of metastable atoms is produced by light which travels only in straight lines. The fact that when the collector is positive the electron currents are also proportional to the light intensity proves that the electrons owe their origin not to photoelectric effect from the electrodes, but to the production of metastable atoms or excited atoms. Small disk-shaped collectors have also been used in which one side, which faces the source of resonance radiation, is covered with mica so that the exposed surface cannot receive radiation, and yet the electron current was nearly as great as if the mica were placed on the back side of the collector, proving that the electron currents are generated by metastable atoms which diffuse short distances to the electrode even when the resonance radiation does not reach the electrode itself.

Since the electrons emitted by the collectors possess considerable initial velocities, and since these electrons make elastic collisions with the neon atoms, it is impossible to obtain a saturation current from these electrodes at these gas pressures, for electrons which diffuse back to the electrodes have sufficient energy to be reabsorbed by it. A theoretical investigation shows that in this case the current i_x that flows between any two electrodes is given by the equation,

$$i_x = \frac{16\pi}{3} I_0 \lambda\, C(V/V_0) \frac{1}{\log(1+V/V_0)}$$

where V is the potential difference between the electrodes, V_0 is the volt equivalent of the velocity with which the electrons are emitted from the cathode, I_0 is the theoretical saturation current density of the electrons emitted from the cathode, λ is the mean free path of electrons, and C is the electrostatic capacitance between the two electrodes (expressed in centimeters). Experiments show that this equation expresses well the volt ampere characteristics of neighboring electrodes in neon exposed to resonance radiation.

Chapter Fourteen

THE CONDENSATION AND EVAPORATION OF GAS MOLECULES

Several years ago, (1) I gave evidence that atoms of tungsten, molybdenum, or platinum vapors, striking a clean, dry glass surface in high vacuum, are condensed as solids at the first collision with the surface. Subsequently, similar evidence (2) was obtained in connection with a study of chemical reactions in gases at low pressures. It was concluded that in general, when gas molecules strike a surface, the majority of them "do not rebound from the surface by elastic collisions, but are held by cohesive forces until they evaporate from the surface." In this way a theory of adsorption was developed (3) which has been thoroughly confirmed by later experiments. It was stated: "The amount of material adsorbed depends on a kinetic equilibrium between the rate of condensation and the rate of evaporation from the surface. Practically every molecule striking the surface condenses (independently of the temperature). The rate of evaporation depends on the temperature (van't Hoff's equation) and is proportional to the *fraction* of the surface covered by the adsorbed material."

R. W. Wood (4) described some remarkable experiments in which a stream of mercury atoms impinges upon a plate of glass held at a definite temperature. With the plate cooled by liquid air, all the mercury atoms condense on the plate, but at room temperature all the atoms appear to be diffusely reflected.

The whole question of the evaporation, condensation, and possible reflection of gas molecules has been discussed at some length in two recent papers (5), (6). It was pointed out that, in Wood's experiments, there are excellent reasons for believing that the mercury vapor actually condenses on the glass at room temperature, but evaporates so rapidly that no visible deposit of mercury is formed. Further evidence of the absence of reflection is furnished by the operation of the 'Condensation Pump' (7).

In a second paper, Wood (8) gives an account of some still more striking experiments. A stream of cadmium atoms, striking the walls of a well exhausted glass bulb, does not form a visible deposit unless the glass is at a temperature below about −90° C. If, by cooling the bulb for a moment with liquid air, a deposit is started, this continues to grow in thickness even after it is warmed to room temperature. From these and similar observations, Wood concludes that:

1. Cadmium atoms all condense on cadmium surfaces at any temperature.
2. Cadmium atoms condense on glass only if it is at a temperature below about −90° C. At higher temperatures, nearly all the atoms are reflected.

This viewpoint leads to no explanation of the changes in the reflection coefficient. The results of Wood's experiments may, however, be explained by the theory that all the atoms, striking either the glass or the cadmium surface, condense, and that subsequent evaporation accounts for the apparent reflection.

Cadmium atoms on a glass surface are acted on by totally different forces from those holding cadmium atoms on a cadmium surface. When a thick deposit of cadmium which has been distilled onto glass in vacuum, is heated quickly above its melting-point, the molten cadmium gathers together into little drops on the surface of the glass. In other words, molten cadmium does not wet glass. Therefore cadmium atoms have a greater attractive force for each other than they have for glass. Thus, single cadmium atoms on a glass surface evaporate off at a lower temperature than that at which they evaporate from a cadmium surface. It is not unreasonable to assume that in Wood's experiments, even at −90° C., the cadmium evaporated off of the glass as fast as it condensed upon it.

This theory possesses the advantage that it automatically explains the apparent reflection of cadmium atoms from a glass surface at room temperature, and indicates why this effect should be absent at low temperatures.

We shall see, moreover, that this condensation-evaporation theory explains many other facts incompatible with the reflection theory.

Let us examine for a moment the essential differences between these two theories. Wood describes his remarkable experimental results, but he has not attempted to discuss the mechanism of the underlying processes. It is clear that Wood uses the term 'reflection' merely to express the fact that under certain conditions no visible deposit is formed when the atoms strike a surface. From this point of view, condensation followed by evaporation is the same as reflection. In considering the possible mechanisms of the process, however, we must sharply distinguish between the two theories.

When an atom strikes a surface and rebounds elastically from it, we are justified in speaking of this process as a reflection. Even if the collision is only partially elastic, we may still use this term. The idea that should be expressed in the word 'reflection' is that the atom leaves the surface by a process which is the direct result of the collision of the atom against the surface.

On the other hand, according to the condensation-evaporation theory, there is no direct connection between the condensation and subsequent evaporation. The chance that a given atom on a surface will evaporate in a given time is not dependent on the length of time that has elapsed since the condensation of that atom. Atoms striking a surface have a certain average 'life' on the surface, depending on the temperature of the surface and the intensity of the forces holding the atom. According to the 'reflection' theory, the life of an atom on the surface is simply the duration of a collision, a time practically independent of temperature and of the magnitude of the surface forces.

To determine definitely which of the two theories corresponds best with the facts, I have repeated Wood's experiments under somewhat modified conditions. A small spherical bulb, together with an appendix containing coconut charcoal, was heated to 600° C. for about four hours while being exhausted by a condensation pump. A liquid-air trap was placed between the pump and the bulb. Some cadmium was purified by distillation and was distilled into the bulb, which was then sealed off from the pump. The cadmium in the bulb was then all distilled into the lower hemisphere. By heating this lower half of the bulb to about 140° C., the upper half remained clear, but by applying a wad of cotton, wet with liquid air, to a portion of the upper hemisphere, a uniform deposit formed within less than a minute and continued to grow, even after the liquid air was removed.

When the liquid air was applied only long enough to start a deposit, it was found in the first experiments that the deposit did not grow uniformly, but became mottled, or showed concentric rings. The outer edges of the deposit were usually much darker than the central portions. By cooling the coconut charcoal in liquid air, this effect disappeared entirely and the cadmium deposits became remarkably uniform in density. It is thus evident that traces of residual gas may prevent the growth of the deposit, particularly in those places which have been the most effectively cooled. This is probably due to the adsorption of the gas by the cooled metal deposit. This gas is apparently retained by the metal, even after it has warmed up to room temperature, so that vapor condensing on the surface evaporates off again at room temperature.

These results indicate how enormously sensitive such metal films are to the presence of gas. However, by using liquid air and charcoal continually during the experiments, most of these complicating factors were eliminated.

If all the cadmium is distilled to the lower half of the bulb and this is then heated to 220° in an oil bath while the upper half is at room temperature, a fog-like deposit is formed on the upper part of the bulb in about fifteen seconds. This deposit is very different from that obtained by cooling the bulb in liquid air. Microscopic examination shows that it consists of myriads of small crystals. According to the condensation-evaporation theory, the formation of this fog is readily understood. Each atom of cadmium, striking the glass at room temperature, remains on the surface for a certain length of time before evaporating off. If the pressure is very low, the chance is small that another atom will be deposited, adjacent to the first, before this has had time to evaporate. But at higher pressures this frequently happens. Now if two atoms are placed side by side on a surface of glass, a larger amount of work must be done to evaporate one of these atoms than if the atoms were not in contact. Not only does the attractive force between the cadmium atom and the glass have to be overcome, but also that between the two cadmium atoms. Therefore the rate of evaporation of atoms from pairs will be much less than that of single atoms. Groups of three and four atoms will be still more stable. Groups of two, three, four, etc., atoms will thus serve as nuclei on which crystals can grow. The tendency to form groups of two atoms increases with the square of the pressure, while groups of three form at a rate proportional to the cube of the pressure. Therefore the tendency for a foggy deposit to be formed increases rapidly as the pressure is raised or the temperature of the condensing surface is lowered.

On the other hand, according to the reflection theory, there seems to be no satisfactory way of explaining why the foggy deposit should form under these conditions.

Experiments show clearly that when a beam of cadmium vapor at very low pressure strikes a given glass surface at room temperature, no foggy deposit is formed, although when the *same quantity* of cadmium is made to impinge against the surface in a shorter time (and therefore at higher pressure) a foggy deposit results. This fact constitutes strong proof of the condensation evaporation theory.

A deposit of cadmium of extraordinary small thickness will serve as a nucleus for the condensation of more cadmium at room temperature. Let all the cadmium be distilled to the lower half of the bulb. Now heat the lower half to 60° C. Apply a wad of cotton, wet with liquid air, to a portion of the upper half for one minute, and then allow the bulb to warm up to room temperature. Now heat the lower half of the bulb to 170° C. In about thirty seconds a deposit of cadmium appears which rapidly grows to a silver-like mirror. This deposit only occurs where the bulb was previously cooled by liquid air.

The question arises: how much cadmium could have condensed on the bulb in one minute while the lower part of the bulb was at 60° C.?

The vapor pressure of cadmium has been determined by Barus (9) between the temperatures 549° and 770° C. If the logarithms of the pressures are plotted against the reciprocals of the temperature, a straight line is obtained from which the following equation for the vapor pressure (in bars) is obtained as a function of absolute temperature

$$\log p = 11.77 - \frac{6060}{T} \tag{1}$$

At 60° C. the vapor pressure of cadmium is of the order of magnitude of 4×10^{-7} bars. Now the number of molecules of gas which strike a square centimeter of surface per second is

$$n = 2.65 \times 10^{19}\, p/\sqrt{MT} \tag{2}$$

Substituting $M = 112$, $T = 333°$, and $p = 4 \times 10^{-7}$, we find that with saturated cadmium vapor at 60° C., $n = 5 \times 10^{10}$ atoms per second per square centimeter.

The maximum number of atoms of cadmium which can condense in *one minute* on a spot cooled in liquid air when the lower part of the bulb is at 60° C. is therefore 3.0×10^{12} atoms per square centimeter. The diameter of a cadmium atom is approximately 3.1×10^{-8} cm., so that it would require 1.0×10^{15} atoms to cover 1 square centimeter with a single layer of atoms.

Therefore the deposit which forms in one minute with the vapor from cadmium at 60°, contains only enough cadmium atoms to cover 3/1000 of the surface of the glass. Yet this deposit serves as an effective nucleus for the formation of a visible deposit.

If the lower part of the bulb is heated to 78° instead of 60°, the nucleus formed by applying liquid air for one minute causes a visible deposit to grow more rapidly (with the lower part of the bulb at 170°). But the nucleus obtained with temperatures above about 78° are not any more effective than those formed at 78°.

A calculation similar to that above shows that the deposit formed in one minute at 78° contains 2.5×10^{13} atoms per square centimeter, or enough to cover 25/1000 of the surface. If we consider that the surface of the glass contains elementary spaces each capable of holding one cadmium atom, the chance that any given cadmium atom will be adjacent to another is $1 - (1 - 0.025)^7$, or 0.16. When the surface is allowed to warm up, the single atoms evaporate, but the pairs remain. The surface is then covered to the extent of 16% of 25/1000, or 4/1000. About 2% of the atoms striking such a surface will fall in positions adjacent to those atoms already on the surface. With cadmium vapor at 170°, 1.4×10^{15} atoms per square centimeter strike the surface each second, so that 2.8×10^{13} would condense in the first second around the 4×10^{12} atoms remaining on the surface. Thus in only a few seconds the whole surface becomes covered with a layer of cadmium atoms. This explains why a surface only partially covered with cadmium atoms can serve so effectively as a nucleus. If a much smaller fraction than 0.025 of the surface is covered, however, there is a long delay in completing the first layer of atoms, so that the visible deposit is formed much more slowly.

The above experiments prove that the range of atomic forces is very small and that they act only between atoms practically in contact with each other. Thus a surface covered by a single layer of cadmium atoms behaves, as far as condensation and evaporation are concerned, like a surface of massive cadmium. This absence of transition layer is in accord with my theory of heterogeneous reactions (10).

One of the best proofs of the correctness of the condensation-evaporation theory was obtained in experiments in which nuclei formed at liquid air temperature, were not allowed to warm up to room temperature, but only to −40° C. In this case the nuclei were formed in one minute from cadmium vapor at 54° C. The nuclei which were kept at −40° C. developed rapidly into cadmium mirrors in cadmium vapor at 170°, while those at room temperature developed extremely slowly. A still more striking demonstration of the theory was obtained when one of the nuclei was allowed to warm up to room temperature and then cooled to −40° before exposure to cadmium vapor at 170°. This nucleus did not develop nearly as rapidly as that which had not been allowed to warm up to room temperature.

These experiments prove that single cadmium atoms actually evaporate off of a glass surface at temperatures below room temperature, although they do not do so at an appreciable rate from a cadmium surface.

This theory affords a very satisfactory explanation of Moser's breath figures on glass and the peculiar effects observed in the formation of frost crystals on window panes. In fact, the theory appears capable of extension to the whole subject of nucleus formation, including, for example, the crystallization of supercooled liquids.

The final paper will be submitted to the *Physical Review* for publication.

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Chapter Fifteen

THE EVAPORATION, CONDENSATION AND REFLECTION OF MOLECULES AND THE MECHANISM OF ADSORPTION

In a recent paper R. W. Wood [1] describes some remarkable experiments in which a stream of mercury atoms is caused to impinge upon a plate of glass held at a definite temperature. With the plate at liquid air temperature all the mercury atoms are condensed on the plate, whereas with the plate at room temperature all the atoms appear to be diffusely reflected. Wood seems to consider that this is a real case of reflection.

There is, however, another way of interpreting the experiments, which, I think, is more in harmony with other facts than that suggested by Wood.

We may, for example, consider that all the atoms of mercury which strike the plate *condense no matter what the temperature of the plate.* When the plate is at the higher temperatures the condensed atoms may reëvaporate again so rapidly that the surface remains practically free from mercury. At first sight it might appear that there is no essential difference between this reëvaporation and a true reflection, but more careful consideration shows that the two phenomena are quite distinct. The difference would be manifest if the so-called reflection were studied at intermediate temperatures. In the case of reflection the number of atoms reflected would always be proportional to the number striking the surface, whereas, according to the reëvaporation theory, the number leaving the surface can never exceed the normal rate at which mercury evaporates into a perfect vacuum.

Wood states that he intends to undertake experiments at intermediate temperatures, and in view of this I should be loath to take up a discussion of the matter at present if it were not for the fact that much of my work during the last few years has had a very direct bearing on the question of the condensation versus the reflection of gas molecules.[2]

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[1] *Phil. Mag., 30,* 300, 1915.

[2] In this connection, for the sake of historical accuracy, attention may be called to the fact that the rectilinear propagation of molecules in vacuo, which Wood and Dunoyer (Comptes Rendus, *152,* 593, 1911) have described, has long been familiar to incandescent lamp manufacturers not only in the case of tungsten lamps, but also with carbon lamps. Professor W. A. Anthony, in a paper read before the American Insti-

As a result of this work, which I shall briefly describe in the following pages, I have gradually become convinced that molecules and atoms of all kinds show little or no tendency to be reflected from a solid surface against which they strike. In the case of metal vapors condensing on the corresponding metals, the evidence seems to indicate that not over one atom per thousand is reflected, if indeed, there is any reflection whatever. However, with molecules of the so-called permanent gases striking surfaces covered with adsorbed films of gas molecules, there is some evidence that a certain amount of reflection may occur. When hydrogen molecules strike a hydrogen covered surface at high temperatures it is possible that as many as 81 per cent. of the molecules are reflected. There is reason to believe that this represents the maximum possible degree of reflection and that with gases other than hydrogen and helium, the amount of reflection is always less than 50 per cent., no matter what may be the nature of the solid surface.

I. EXPERIMENTAL DATA

Evaporation and Condensation.—In connection with an experimental determination of the rate of evaporation of tungsten filaments in a high vacuum [3] the following relation between the vapor pressure p and the rate of evaporation m (in grams per sq. cm. per second) was derived from the principles of the kinetic theory

$$m = (1 - r)\sqrt{\frac{M}{2\pi RT}}\,p. \tag{1}$$

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tute of Electrical Engineers at New York in 1894, described this phenomena as follows (Trans. Amer. Inst. Elect. Eng., *11*, 142, 1894) : "In the old Edison lamps the filament was copper-plated to the platinum wires. When a break in the filament occurred near the junction, the arc vaporized the copper and covered the bulb with a coating of metallic copper, except that a line of clean glass was often left on the side opposite the break, the line being the shadow of the unbroken leg of the filament. . . . The plain old-fashioned unpretentious vapor tension that bursts our steam boilers is all-sufficient to account for this rectilinear projection across the lamp bulb when there is nothing in the way." In the very active discussion which followed, Professor Elihu Thomson said "I am confident that I have seen it (this phenomenon) in series lamps when the carbon broke. In a good vacuum the carbon vapor condensing would give rise to particles which would move in rectilinear paths. The shadow effect is dependent on a *local* evolution of vapor, with a part of the wire or filament between the point of evolution and the opposite glass surface. I am also confident that I have seen platinum shadows." In the further discussion, J. W. Howell said, "The molecules of carbon set free by evaporation, fly from the filament as Professor Anthony says, in straight lines. They are projected from every part of the filament and . . . cast shadows on the globes. The reason why they do not cast shadows in most lamps is that the filament is not all in one plane." Mr. Howell then exhibited to those present, both carbon and platinum lamps which showed distinct shadows.

[3] Langmuir, *Phys. Rev.*, *2*, 329, 1913, and *Phys. Zeitsch.*, *14*, 1273, 1913.

Here M is the molecular weight of the vapor, R is the gas constant, and r is the coefficient of reflection of the vapor molecules which strike the surface of the solid (or liquid). It was stated at that time (1913) that "There are good reasons for believing that the reflection of vapor molecules from the surface takes place to a negligible degree only," and there followed a discussion of Knudsen's results on the heat conductivity of gases at low pressures which we shall consider in more detail below.

The above formula, taking $r = 0$, was then used to calculate the vapor pressure of tungsten from the experimental data on the rate of evaporation.

Very recently, however, Knudsen[4] has accurately determined the rate of evaporation of mercury in a high vacuum, and by comparing this with the vapor pressure, using an equation similar to (1), he has been able to prove conclusively that, with a clean mercury surface, r does not exceed one per cent. That is, he finds that all the mercury atoms striking a mercury surface are condensed when the surface is at room temperature.

This result of Knudsen's, together with Wood's conclusion that reflection is absent when the glass plate is at the temperature of liquid air, indicates that there is little or no reflectivity of mercury atoms from either a solid or liquid surface of mercury.

Experiments on the formation of "shadows" in the evaporation of filaments in a high vacuum have proved that at least for surfaces at room temperature the same conclusion may be drawn regarding the reflectivity of atoms of tungsten, platinum, copper, gold, silver, molybdenum, carbon, iron, nickel and thorium.

The reflectivity of metal atoms striking surfaces of the same metals at room temperature (or lower) is zero.

The question remains whether the reflectivity is still zero when the surfaces are at higher temperatures and when surfaces other than that of the metal are concerned. Knudsen's work with mercury has shown that the reflectivity with this metal remains zero even at temperatures where the vapor pressure of the metal becomes fairly high.

We shall see, however, from a consideration of other cases, that the coefficient of reflectivity changes very little if at all with temperature, so that I think the above rule may safely be generalized to include metal vapors condensing on metals at any temperature.

Whether or not the same rule would apply to non-metallic substances with equal accuracy, is rather doubtful. However, we shall see from theoretical considerations that even in such cases as that of hydrogen atoms striking a surface of liquid or solid hydrogen, there is reason to believe that the amount of reflection is small.

[4] *Ann. Phys., 47,* 697, 1915.

HEAT CONDUCTION IN GASES AT LOW PRESSURES

Kundt and Warburg in 1875 predicted from the kinetic theory that there should be a discontinuity in the temperature close to the surface of a solid body which is dissipating heat by conduction into a gas at low pressure. Smoluchowski, in 1898, observed and studied this phenomenon and developed the theory of it. He found that in some gases, particularly hydrogen, the amount of heat given up to the gas by the solid was only a fraction of that which should be delivered if each molecule striking the surface reached thermal equilibrium with it before leaving.

Knudsen[5] gave the name "accommodation coefficient" to the ratio of the heat actually carried away by the gas, to that which would be carried if thermal equilibrium were reached. Kudsen measured the accommodation coefficient (α) for several gases and several different kinds of surface. The lowest value found was with hydrogen in contact with a polished platinum or glass surface, in which case Knudsen obtained $\alpha = 0.26$. With heavier gases, such as nitrogen and carbon dioxide, he found $\alpha = 0.87$.

Soddy and Berry[6] in a similar study of the heat conductivity of gases at low pressures, found that α for hydrogen in contact with platinum varied from 0.25 at $-100°$ C. to 0.15 at $+200°$. For argon they found an average value $\alpha = 0.85$, while for helium they found 0.49 at $-100°$ C. and 0.37 at $+150°$ C. The accommodation coefficients obtained with heavier gases were always close to unity.

The writer[7] has determined the accommodation coefficient of hydrogen in contact with tungsten at 1500° K. and obtained $\alpha = 0.19$, while nitrogen under the same conditions gave $\alpha = 0.60$.

The evidence thus far available indicates that the accommodation coefficients of the ordinary gases range from 0.19 up to unity. Only in the cases of hydrogen and helium have accommodation coefficients less than 0.8 been found at room temperature. It is interesting to note that all observers find that the coefficient for a given gas is independent of the nature of the solid, so long as it has a polished surface. This is an indication, for which other evidence will be given below, that the surfaces under the conditions of the experiments are covered with adsorbed layers of gases.

Another conclusion from the experiments is that the accommodation coefficient varies only slightly with the temperature, there being a tendency for it to decrease at higher temperatures. Thus for hydrogen the coefficient seems to decrease from about 0.35 at $-190°$ to 0.19 at 1500° K. With both helium and nitrogen there is a slight tendency for α to decrease with rising temperature.

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[5] *Ann. Phys., 34,* 593, 1911.

[6] *Proc. Roy. Soc., 84,* 576, 1911.

[7] *Jour. Amer. Chem. Soc., 37,* 425, 1915.

The probable relationship between the accommodation coefficient and the reflectivity of molecules from surfaces will be discussed below, together with other experimental data.

THE "SLIP" IN GASES AT LOW PRESSURES

The viscosity effect analogous to the temperature discontinuity at a surface has been called the "slip." This effect, first observed by Kundt and Warburg, has been the subject of much recent study. Knudsen[8] calculates the coefficient of slip on the assumption that the molecules striking any surface are emitted from it in directions which are absolutely independent of the original directions of incidence. By elaborate experimental investigations Knudsen obtains confirmation of his theoretical conclusions and thus justifies his assumptions. Smoluchowski[9] Timiriazeff,[10] Gaede,[11] and Baule,[12] however, conclude, on experimental and theoretical grounds, that the directions of the emitted molecules are not entirely independent of the directions of the incident molecules.

It is of interest to note that Gaede, as a result of extremely careful experimental work, concludes that the amount of specular reflectivity is negative. That is, he finds at pressures above .001 mm., and up to 20 mm., that the amount of gas which flows through a tube is *less* than that calculated by Knudsen on the assumption of completely irregular reflection. Gaede draws the conclusion that a certain fraction (sometimes as large as 50 per cent.) of the incident molecules tend to return after collision in the direction from which they came. The other observers, however, all find that the amount of gas flowing through tubes is greater than that calculated by Knudsen's formula.

Knudsen, on the other hand,[13] carried out further measurements with hydrogen at low pressures and found that there cannot be a specular reflection of hydrogen molecules amounting to more than about one per cent.

Millikan[14] has calculated the coefficient of slip from his measurements on the fall of small spheres and has concluded that the slip in air is about 10 per cent. and in hydrogen about 8 per cent. greater than would be expected, according to Knudsen's assumption regarding the absence of specular reflection.

The experimental evidence on the slip of gases at low pressures does not throw much light on the reflectivity of gas molecules, but if Millikan's interpretation of his experiments is correct they would seem to indicate that a reflectivity as high as 10 per cent, occurs in some cases.

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[8] *Ann. Phys., 28,* 75, 1908.

[9] *Phil. Mag., 46,* 199, 1898.

[10] *Ann. Phys., 40,* 971, 1913.

[11] *Ann. Phys., 41,* 289, 1913.

[12] *Ann. Phys., 44,* 145, 1914.

[13] *Ann. Phys., 35,* 389, 1911.

[14] Discussion before the American Phys. Soc., Chicago, Nov. 30, 1915.

STATISTICS OF CHEMICAL REACTIONS

(*a*) *Heterogeneous Reactions.*—The rate at which the molecules of a gas come into contact with a solid surface immersed in it, may be calculated by equation (1). Suppose a heterogeneous chemical reaction occurs at the surface of the solid body. Then, if we can measure the rate at which the reaction occurs, we may be able to calculate by Equation 1 what fraction of the collisions between the gas molecules and the solid body results in a chemical reaction. Let us call this fraction ε.

In order to avoid complications due to the accumulation of the products of the reaction close to the surface it will be necessary either to work with very low pressures of gases or to choose reactions which take place very slowly.

The value of ε may in general have any value less than unity. It is evident that the reflectivity of the gas molecules striking the surface must be less than $1 - \varepsilon$ and therefore, by a determination of ε, we obtain an upper limit for the reflectivity.

Strutt[15] has measured ε for two heterogeneous reactions. In the decomposition of ozone in contact with a silver surface he found ε equal to unity, while in the case of the conversion of atomic nitrogen into molecular nitrogen in contact with copper oxide, he obtained $\varepsilon = .002$. From this we may conclude that the reflectivity of ozone molecules from a silver surface is small. In the second case, however, it is not necessary to conclude that the reflectivity is 0.998. We shall see from the general discussion below that the small value of ε is probably caused by a large portion of the surface being in an inactive condition, perhaps due to its being covered with a layer of adsorbed nitrogen molecules.

In a study of the rate of attack of a heated tungsten filament by oxygen at low pressure,[16] the writer determined the values of ε for the reaction $2W + 3O_2 = 2WO_3$. The fraction ε was found to be independent of the pressure and to increase rapidly with temperature from .001 at 1270° K. to 0.15 at 2770° K.

Some recent work has shown that at higher temperatures ε continues to increase so that at 3000° K. it is over 0.40. Extrapolation indicates that at still higher temperatures ε would reach a limiting value of about 0.7.

From these results we may conclude that the reflectivity of oxygen molecules from heated tungsten does not exceed 30 per cent. It is probable in this case also, that the small values of ε at low temperatures are caused by an inactive condition of the greater part of the surface, rather than by a change in the reflectivity.

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[15] *Proc. Roy. Soc., A., 87,* 302, 1912.

[16] *Jour. Amer. Chem. Soc., 35,* 115, 1913.

Experiments on the oxidation of molybdenum filaments have led to similar conclusions in regard to the reflection of oxygen molecules.

When a wire of tungsten, or other metal capable of withstanding high temperature, is heated to 1500° K. in hydrogen at low pressure, a part of the hydrogen is converted into atomic hydrogen.[17] At very low pressures this active modification of hydrogen can diffuse long distances through glass tubing at ordinary temperatures,[18] but cannot pass even short distances through tubing cooled by liquid air.

When one considers that the pressures employed in these experiments were so low that the normal free path would be of the order of several meters, it is evident that the reflectivity of hydrogen atoms from glass surfaces cooled in liquid air must be very small, if not actually zero. With the glass at room temperature the reflectivity is probably also negligible, but the atoms then reëvaporate more rapidly and are thus able to travel considerable distances.

In connection with a quantitative study of the degree of dissociation of hydrogen at various temperatures, it has been shown [19] that *every hydrogen atom* striking a pure tungsten surface (at 2000–3500° K.) condenses and that 68 per cent. of all hydrogen molecules striking the surface condense.

When the tungsten filament was heated to a temperature over 2700° K. in hydrogen at a pressure below 200 bars, it was found that 68 per cent. of all the molecules striking the filament were dissociated and that this fraction remained unchanged even when the filament temperature was raised several hundred degrees higher.

The fact that this coefficient (0.68) is larger than the accommodation coefficient found for a tungsten wire at 1500° in hydrogen (0.19) requires some explanation. It seems at first sight paradoxical that 68 per cent. of the molecules reach chemical equilibrium and are dissociated, whereas at lower temperatures only 19 per cent. reach thermal equilibrium before leaving the surface. In a recent paper [20] the writer gives independent evidence that at lower temperatures the tungsten surface is practically completely covered with a layer of hydrogen molecules, whereas at higher temperatures only a minute fraction of the surface is so covered. Thus the coefficient 0.19 applies to hydrogen molecules striking a surface already covered with an adsorbed layer of hydrogen molecules, while the coefficient 0.68 applies to hydrogen molecules striking an absolutely clean tungsten surface.

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[17] Langmuir, *Jour. Amer. Chem. Soc.*, *34*, 1310, 1912.

[18] Freeman, *Jour. Amer. Chem. Soc.*, *35*, 927, 1913.

[19] Langmuir, *Jour. Amer. Chem. Soc.*, *37*, 457, 1915.

[20] *Jour. Amer. Chem. Soc.*, *38*, 1145, 1916.

Some interesting data on the reflectivity of molecules from a platinum surface have been obtained in connection with a study of the combustion of hydrogen and carbon monoxide at low pressures in contact with a heated platinum wire.[21] In these experiments a platinum filament was mounted in the center of a spherical bulb of four liters' capacity, provided with an appendix (10 cm. long and 3 cm. in diameter) which was cooled by liquid air. This bulb was connected through a liquid air trap to a McLeod gage and a system for the quantitative analysis of small quantities of gas (of the order of one cubic mm.). Low pressures of mixtures of oxygen with either hydrogen or carbon monoxide were introduced into the bulb and the filament heated to a definite temperature. The products of the reaction, water vapor or carbon dioxide, were condensed in the appendix and thus prevented from returning to the filament. The pressures employed ranged from 0.1 up to 30 bars, so that the mean free path of the molecules was many times greater than the diameter of the filament. The velocity of the reaction was determined by taking readings of the gage at regular intervals.

With filament temperatures up to about 500–700° K., it was found that the reaction velocity increased rapidly with temperature. The rate was proportional to the partial pressure of oxygen, and *inversely proportional* to the pressure of hydrogen or carbon monoxide. Thus with an excess of oxygen the reaction started slowly, and as the proportion of combustible gas decreased, the rate increased until it became practically infinite (too rapid to measure). From this it may be concluded that hydrogen and carbon monoxide are negative catalyzers or catalytic poisons. Evidently these substances cannot prevent the reaction on the surface unless they are present on the surface. It thus follows that a surface of platinum at temperatures up to 500–700° K. in pressures of hydrogen or carbon monoxide, as low as one bar, is practically completely covered with an adsorbed film of these gases.

When the temperature of the platinum was raised, the reaction became so rapid that with a filament having a surface of 0.31 sq. cm., the pressure in the four liter bulb in some cases fell to half value in less than 6 seconds. To lower this rate a new filament (length 0.7 cm., diameter .003 cm.), having a surface of only .0067 sq. cm., was substituted for the old one.

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[21] A preliminary account of these experiments, giving only qualitative results, was published in the *Jour. Amer. Chem. Soc.*, *37*, 1162, 1915. The complete data on these experiments, together with that on several other similar reactions, will probably be published in the same journal.

Under these conditions the velocity of the reaction could be followed up to the melting point of the filament.

With carbon monoxide the reaction velocity reaches a maximum when the filament temperature is about 900° K. and apparently becomes negligibly small in comparison, when the temperature is raised to 1300° K. or higher.

With hydrogen, the rate of reaction also reaches its maximum value at about 900° K. This rate does not decrease at higher temperatures, however, but remains practically constant up to the melting point of the filament.

From equation (1) the rate at which each gas comes into contact with the filament may be calculated. By comparing this with the actual rate at which the gas enters into reaction it is possible to determine ε. Out of all the hydrogen (or carbon monoxide) molecules which strike the filament in a given time, let ε_1 represent the fraction which reacts with the oxygen. Similarly let ε_2 be the corresponding fraction for the oxygen molecules striking the surface. The following table gives the values of ε_1 and ε_2 calculated directly from the experimentally determined maximum rates of reaction.

In this table p_1 is the partial pressure of hydrogen or carbon monoxide in bars and p_2 is that of the oxygen. We see that when hydrogen is in large excess, 53 per cent. of all oxygen molecules which strike the filament react with hydrogen to form water. This may happen in either one or two ways:

Reaction $2H_2 + O_2 = 2H_2O$:

p_1	p_2	ϵ_1	ϵ_2
bars	bars		
20.0	4.2	.06	.53
1.3	11.5	.41	.09

Reaction $2CO + O_2 = 2CO_2$:

p_1	p_2	ϵ_1	ϵ_2
12.6	0.7	.02	.18
1.4	0.7	.19	.20
1.4	12.0	.31	.02

1. The oxygen may react with hydrogen already present on the surface.
2. The oxygen may condense on the surface and react with hydrogen molecules which subsequently strike the surface.

In either case the reflectivity of the oxygen molecules cannot exceed 47 per cent. (100 − 53). Similarly we may conclude that the reflectivity of hydrogen molecules is not greater than 59 per cent.

The values for ε given in the above table are to be looked upon as lower limits. No correction was made for the cooling effect of the leads, which was very considerable with the short filament used. This correction would be much more important in the case of the combustion of carbon monoxide, since with this reaction the maximum velocity occurs only over a narrow range of temperature. Furthermore, traces of carbon dioxide were found to slightly poison the surface of the platinum, so that the catalyzer only slowly recovered its full activity. It may well be that minute traces of impurities have made the values of ε lower than they should be under ideal conditions.

From these considerations it seems probable that the values of ε corresponding to perfectly pure gases and a filament at uniform temperature, might approach unity as a limit in the case of each of three gases.

These experiments indicate that the reflectivity of oxygen, hydrogen, and carbon monoxide molecules is small even at temperatures of 900° K. There is every reason to believe that the reflectivity at room temperature is not greater than at higher temperatures.

A large number of other heterogeneous reactions are being studied by similar methods and the coefficients ε are being determined. All of this work so far seems to bear out the general conclusion that values of ε much less than unity occur only where the surface of the solid is largely covered by some inactive material. The velocity of the reaction is thus determined by that *fraction of the surface* which is active.

(b) Homogeneous Reactions.—Although homogeneous reactions furnish no direct evidence regarding the reflectivity of molecules from solid surfaces, yet several cases that have been studied have indicated that reactions are by no means rare in which *every* collision between unlike molecules *results in combination.* In this case we may consider that the reflectivity between the molecules is negligible, and are thus led to suspect that in many gas reactions, when two molecules collide, they stick to each other (condense), although they may subsequently separate again (evaporate).

When a tungsten filament is heated to 2800° K. in vacuum, it evaporates at the rate of 0.43×10^{-6} grams per sq. cm. per second.[22] If the filament is surrounded by nitrogen at a pressure less than 500 bars, the rate of evaporation remains unchanged, but each *atom* of tungsten vapor combines on its first collision with a nitrogen molecule to form the definite chemical compound WN_2, which collects on the bulb as a brown deposit. The nitrogen therefore disappears at the constant rate (independent of pressure) of .057 cubic mm. of nitrogen (at 1 megabar) per sec. per sq.

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[22] Langmuir, *Phys. Rev.*, *2*, 340, 1913.

cm. of tungsten surface. As the temperature of the filament is raised the rate of disappearance of nitrogen increases exactly in proportion to the rate of evaporation of the tungsten.

In a similar way it has been found[23] that tungsten atoms combine on the first collision with carbon monoxide molecules to form WCO, and that platinum atoms combine on the first collision with oxygen molecules to form PtO_2.

A remarkable case is that of molybdenum and nitrogen. There is definite evidence[24] that each collision between an atom of molybdenum and a molecule of nitrogen results in combination, but there are apparently two kinds of compound formed. One is a stable chemical compound which, when it deposits on the bulb, cannot be decomposed by heating to 350° C., while the other is an extremely unstable compound which decomposes spontaneously when it strikes the bulb. The stable compound tends to be formed in larger amount when the velocity of impact of the molybdenum atom and the nitrogen molecule is *small;* that is when either the bulb temperature or the filament temperature is low. On the other hand, a high velocity of impact (high temperature of bulb or filament) favors the formation of the unstable substance.

There are indications of a similar behavior when a tungsten filament is heated to a very high temperature (3000° K. or more) in hydrogen at low pressure, only in this case the compounds formed are less stable.

II. THEORETICAL CONSIDERATIONS

The phenomena of condensation, evaporation and reflection of molecules are closely related to those of the viscosity, heat-conductivity and adsorption of gases at low pressures.

Various hypotheses regarding the mechanism of these phenomena have been proposed. Maxwell[25] in considering the surface conditions of a gas in contact with a moving solid, assumed that "of every unit of area a portion f, absorbs all the incident molecules, and afterwards allows them to evaporate with velocities corresponding to those in still gas at the temperature of the solid, while a portion $(1 - f)$ perfectly reflects all the molecules incident upon it."

Smoluchowski[26] used a similar hypothesis in regard to the temperature drop near a surface in a gas at low pressure. He also suggested a second hypothesis, namely. When molecules of a temperature T_1 strike a surface at a higher temperature T_2, the molecules leaving the surface have a temperature T intermediate between T_2 and T_1 such that

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[23] *Jour. Amer. Chem. Soc., 37,* 1159, 1915.

[24] *Jour. Amer. Chem. Soc., 37,* 1157, 1915.

[25] *Phil. Trans., 170,* 249, 1879.

$$T - T_1 = \alpha(T_2 - T_1), \tag{2}$$

where α is a number less than unity which has subsequently been called "accommodation coefficient" by Knudsen.

Smoluchowski considered that the same value of f or α could be applied to the phenomena of both viscosity and heat conductivity and thus calculated a relation between the coefficient of slip and the temperature drop at the surface.

Knudsen (*l. c.*), on the other hand, considered α to be unity in the case of viscosity, although not in the case of heat conduction.

Baule[27] attempts to solve this difficulty by analyzing the probable mechanism by which heat or momentum is transferred from gas to solid. Baule assumes that the solid consists of a cubic space lattice of elastic spherical molecules or atoms which are vibrating about their equilibrium positions with a mean kinetic energy corresponding to the temperature of the solid.

The molecules of the gas strike against those of the solid and rebound from them according to the laws of elastic collision. If E_1 be the mean kinetic energy of the incident molecules, E_2 the mean energy of the molecules of the solid, and E' the mean energy of the gas molecules after one collision with the molecules of the solid, then

$$E' = \beta E_1 + (1 - \beta)E_2, \tag{3}$$

where

$$\beta = \frac{m_1{}^2 + m_2{}^2}{(m_1 + m_2)^2}. \tag{4}$$

Here m_1 is the mass of the gas molecules and m_2 is that of the molecules of the solid.

It is evident that many of the molecules make more than one collision before leaving the solid surface. Baule assumes that, of all the molecules striking the surface, the fraction ν make only one collision, while the fraction $1 - \nu$ are absorbed and thus make such a large number of collisions that they reach complete equilibrium with the solid before leaving it again.

Thus, if E is the mean energy of all the molecules leaving the surface we have

$$E = \nu E' + (1 - \nu)E_2, \tag{5}$$

whence from (3)

$$E = \beta\nu E_1 + (1 - \beta\nu)E_2. \tag{6}$$

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[27] *Ann. Phys., 44,* 145, 1914.

Since the mean energy of molecules is proportional to their temperature Equation 6 may be written

$$T = \beta\nu T_1 + (1 - \beta\nu)T_2, \tag{7}$$

or

$$(T - T_1) = (1 - \beta\nu)\ (T_2 - T_1). \tag{8}$$

By comparing this equation with (2) it is seen that they are of the same form and that $(1 - \beta\nu)$ has the same significance as Knudsen's accommodation coefficient.

In a similar manner Baule calculates the coefficient of slip. Let v_1 be the average velocity component, parallel to the surface, of the incident molecules; v_2 the tangential velocity of the surface in the same direction, and v' be the average velocity (parallel to the surface) of the gas molecules which rebound from the surface after one collision. Baule shows that

$$v' = \gamma v_1 + (1 - \gamma)v_2, \tag{9}$$

where

$$\gamma = \frac{m_1}{m_1 + m_2}. \tag{10}$$

Of all the molecules striking the surface, the fraction ν make only one collision and are thus reflected with the velocity component given by (9), whereas the fraction $(1 - \nu)$ are absorbed and thus finally leave the surface with the average velocity component v_2. If v be the average velocity component parallel to the surface of *all* the molecules leaving it, then

$$v = \nu v' + (1 - \nu)v_2, \tag{11}$$

whence from (9)

$$v = \gamma\nu v_1 + (1 - \gamma\nu)v_2 \tag{12}$$

or

$$(v - v_1) = (1 - \gamma\nu)\ (v_2 - v_1). \tag{13}$$

The accommodation coefficient for viscosity is thus $(1 - \gamma\nu)$ instead of the $(1 - \beta\nu)$ which applies to heat conductivity. Thus Baule shows that there is no theoretical justification for Smoluchowski's assumption that the coefficients for heat conduction and viscosity are the same.

In the case of hydrogen in contact with a platinum surface we have $m_1 = 2$ and $m_2 = 195$, whence by (4) and (10), $\beta = 0.98$ and $\gamma = .01$. If we take Knudsen's value $\alpha = 0.26$ for the accommodation coefficient (heat conduction), we find $1 - \beta\nu = 0.26$, whence $\nu = 0.76$. From this we obtain $(1 - \gamma\nu) = 0.992$, which should be the accommodation coefficient for viscosity. This is in good agreement with Knudsen's experiments from which he concludes that the directions of the reflected molecules are independent of those of the incident molecules; in other words, that $\alpha = (1 - \gamma\nu) = 1.00$.

If we consider the case of argon in contact with platinum, for which Soddy and Berry found $\alpha = 0.85$, we obtain:

$$\begin{aligned} m_1 &= 40, \\ m_2 &= 195, \\ \alpha &= 0.85, \\ \beta &= 0.72, \\ \gamma &= 0.17, \\ 1 - \beta\nu &= 0.85, \\ 1 - \gamma\nu &= 0.965. \end{aligned}$$

The accommodation coefficient for viscosity thus decreases with increasing density of the gas, but remains nearly equal to unity.

The experimental work on slip has shown that the accommodation coefficient for viscosity is nearly unity, but the accuracy of the results has not yet been sufficient to determine whether the values calculated by Baule's theory are correct.

Baule attempts to calculate the coefficient ν by making various assumptions as to the manner in which the molecules on the surface are "shadowed" by others, but the validity of the assumptions seems so doubtful that the resulting equations have little more value than empirical equations.

On the whole, Baule's theory marks a distinct advance in our understanding of the mechanism of the exchange of energy between a gas and a solid, but closer consideration of the assumptions underlying Baule's theory shows that they cannot correspond to the facts.

Baule fails to take into account the attractive forces between the atoms, although it is evident that such forces must be of prime importance in determining the amount of condensation and reflection. The phenomena of cohesion, condensation and adsorption are all manifestations of these attractive forces, and Sutherland[28] has shown that even in the gaseous state the attraction between molecules considerably decreases their mean free path.

We know from the work of Bragg and others that the atoms of crystals are arranged according to a space lattice structure in which the identity of molecules usually disappears.

In a crystal of sodium chloride the forces holding the crystal together evidently act between adjacent sodium and chlorine atoms; in other words, they are of the nature of what we have usually called chemical forces.

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[28] *Phil. Mag.*, *36*, 507, 1893.

In a diamond crystal the carbon atoms form an endless chain of benzol rings, and the stability of this chemical group is probably the cause of the hardness, high melting-point and low vapor pressure of solid carbon. There is every reason to assume that all forces acting between the atoms of solid bodies are qualitatively of the same nature. The inert gases crystallize at low temperatures, so that even with these substances the atoms are surrounded by force fields which are only quantitatively different from those of more chemically active substances.

In the case of the diamond the arrangement of the atoms corresponds to the tetravalent character of the carbon atom, but in most crystals the valency of the atoms appears to be *divided* between several other atoms. Thus in the sodium chloride crystal the single valency of the sodium is divided between six chlorine atoms.

The principal characteristics of chemical forces are that they act only through very short distances and that they show in a marked degree the phenomena of saturation. Thus chemical forces act only between *adjacent* atoms, and even then only when the distances between the atoms are of the order of magnitude of the diameter of the atoms. When an atom of oxygen has taken up two hydrogen atoms it loses its attraction for other hydrogen atoms: it becomes chemically saturated. However, from the fact that water molecules become associated $(H_2O)_n$ and readily combine with substances as water of crystallization, we may conclude that the presence of two hydrogen atoms around an oxygen atom does not entirely saturate the chemical forces. Werner's theory of valence recognizes the existence of residual valences.

In a crystal the forces of attraction must be balanced by repulsive forces. We cannot assume that the repulsive forces are exerted only during collisions between adjacent atoms but, because of the work of Einstein,[29] Lindemann [30] and others, must assume that the atoms oscillate about positions of equilibrium in which the attractive and repulsive forces balance.

The atoms on the surface of a crystal must also be held by attractive and repulsive forces, so that they oscillate about equilibrium positions, but these atoms must be looked upon as being in an unsaturated state. There is every reason, therefore, for the existence of very strong attractive forces within a short distance of the surface of solid bodies. The phenomena of adsorption may be looked upon as a result of these unsaturated chemical forces. This will be discussed in more detail in Part II. of this paper.

[29] *Ann. Phys.*, *34*, 170, 1911, and *35*, 679, 1911.

[30] *Phys. Ztschr.*, *11*, 609, 1910.

By the aid of the viewpoint developed above, let us analyze more closely the probable mechanism of condensation, reflection and evaporation of atoms or molecules.

If an atom (or molecule) A approaches the surface of a solid body, it will be subjected to an attractive force as soon as it comes within a certain distance of the surface. This force will increase in intensity as A approaches nearer the surface, will pass through a maximum and will then decrease to zero when A reaches the equilibrium position. The work done by the attractive forces will have been converted into kinetic energy, part of which is possessed by the atom and the remainder of which is divided among atoms forming the surface.

The kinetic energy of A will carry it past the equilibrium position into a region in which it is subjected to a repulsive force. The component of its velocity toward the surface will thus decrease to zero. It will then be driven back through the equilibrium position, and if its outward velocity is sufficient it may escape from the region of attractive forces and travel indefinitely away from the surface. On the other hand, if its velocity is not great enough to enable it to escape, it will describe a complex orbit and, by loss of energy to adjacent atoms, will finally oscillate about its equilibrium position with a mean kinetic energy corresponding to the temperature of the surface.

The amount of work done by the attractive forces upon an atom A while it moves to an equilibrium position is measured by the heat of evaporation or adsorption and is equal to λ/N, where λ is the internal heat of evaporation per gram molecule and N is equal to 6.062×10^{23}. In the case of adsorption of a gas by a solid λ represents the heat of adsorption.

If the attractive and the repulsive forces were both exerted by a single atom of the solid, and if this atom could move freely towards the incident atom, then we should be justified in treating the problem as if attractive forces were absent and elastic collisions occurred. In this case we could apply Baule's results directly.

But it is almost certain that the attractive forces are exerted by several atoms. Bragg has found that among metals the face centered cubic lattice structure is the most common. In this lattice each atom is surrounded by twelve others equally spaced from it. An atom on the surface must then usually have from four to eight other atoms exerting force on it. On the other hand, it is very probable that an atom which passes through the equilibrium position with high velocity would be subjected to repulsive forces exerted principally by *one* atom of the solid. This would naturally follow from the fact that the repulsive force must increase with the proximity to an atom much more rapidly than the attractive force decreases on receding from the equilibrium position.

In order to be able to estimate the magnitude of the effects produced by this difference in the origin of the attractive and repulsive forces, let us consider the case of the following model:

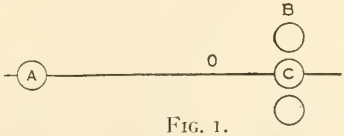

FIG. 1.

In Fig. 1, let A be an atom of mass m_1 which is attracted by a group of atoms B, each of mass m_2. Consider that all the atoms are elastic spheres initially at rest. Let O be the common center of gravity of all the atoms. Then the atoms will all move toward O. If we consider the one dimensional problem only, then we may assume that A will collide with *one* of the atoms B (say C) at the point O, and those two atoms will continue to move along the line AO. Let n be the number of atoms in the group B, excluding C, the one which collides with A. If V_1 and V_2 are the velocities (all measured from left to right) of A and C respectively just before their collision, and V_1' and V_2' are the velocities just after their collision, then we have by the principles of the conservation of energy and momentum:

$$m_1 V_1^2 + m_2 V_2^2 = m_1(V_1')^2 + m_2(V_2')^2, \tag{14}$$

$$m_1 V_1 + m_2(1 + n) V_2 = 0, \tag{15}$$

$$m_1 V_1 + m_2 V_2 = m_1 V_1' + m_2 V_2'. \tag{16}$$

Let the ratio of the velocity of A before and after the collision be β, thus

$$\beta = \frac{V_1'}{V_1} \tag{17}$$

and let

$$\gamma = \frac{m_1}{m_2}. \tag{18}$$

If we substitute these in equations (14), (15) and (16) and solve for β,

$$\beta = \frac{\gamma n \pm (\gamma + n + 1)}{(n + 1)(\gamma + 1)}. \tag{19}$$

For the case in hand it can be readily seen that we should take the negative sign. Equation (19) thus becomes:

$$\beta = -\frac{1 + \gamma\left(\frac{1 - n}{1 + n}\right)}{1 + \gamma}. \tag{20}$$

If $n = 0$, this gives $\beta = -1$, so that the atom A has its velocity reversed. Thus when $n = 0$ the existence of attractive forces between the atoms does not change the conditions from those of elastic collisions. If, however, $n = 1$ we find

$$\beta = -\frac{1}{1+\gamma},$$

so that the velocity after collision is much less than we would calculate according to the laws of elastic collision.

This loss in velocity, which Baule has failed to take into account, would result in a very great decrease in the number of atoms reflected from the surface. In order to estimate the effect on the reflectivity we need to consider the initial velocity of the atom A, due to its thermal energy.

We may calculate this effect approximately by considering two atoms A and C having given initial velocities, but without attractive force between them. Let the initial velocities of A and C be v_1 and v_2 respectively. Let v_0 be the velocity of the common center of gravity of A and C and let v_1' be the velocity of A after collision.

Then

$${}_0 = \frac{m_1v_1 + m_2v_2}{m_1 + m_2} = \frac{\gamma v_1 + v_2}{\gamma + 1} \qquad (21)$$

The velocity of A towards the center of gravity is $v_1 - v_0$ before collision. After collision this velocity is reversed. The actual velocity of A after collision v_1' is thus equal to $-(v_1 - v_0) + v_0$. This gives, with

$$v_1' = \frac{\gamma v_1 + 2v_2 - v_1}{1 + \gamma} \qquad (22)$$

Let us now return to the consideration of an atom striking a surface toward which it is attracted. We have seen that the work done by the attractive forces in bringing the atom to an equilibrium position is λ/N. This appears as kinetic energy of the atom $\frac{1}{2}m_1V_1^2$. If M_1 is the molecular weight of the atom or molecule A, then since $M_1 = Nm_1$

$$V_1 = \sqrt{\frac{2\lambda}{M_1}}. \qquad (23)$$

After collision with the atom C the velocity of A will be

$$V_1' = \beta\sqrt{\frac{2\lambda}{M_1}}.$$

But because of the initial velocities of A and C the velocity V_1' should be increased (approximately) by v_1', so that the velocity of A, upon returning to the equilibrium position, will be

$$\beta\sqrt{\frac{2\lambda}{M_1}} + v_1'.$$

The condition that the atom may just be able to escape from the surface is that this velocity shall be equal to $-\sqrt{2\lambda/M_1}$, in other words, the condition is

$$v_1' = -(1+\beta)\sqrt{\frac{2\lambda}{M_1}}. \tag{24}$$

Now let α_1 and α_2 be the ratios between the initial velocities of A and C respectively, and the mean velocities due to thermal agitation. Thus,

$$\alpha_1 = \frac{v_1}{\bar{v}_1} \quad \text{and} \quad \alpha_2 = \frac{v_2}{\bar{v}_2}, \tag{25}$$

where the mean velocities of thermal agitation $\bar{v}_1$ and $\bar{v}_2$ are given by

$$\bar{v}_1 = \sqrt{\frac{3RT_1}{M_1}} \quad \text{and} \quad \bar{v}_2 = \sqrt{\frac{3RT_2}{M_2}}. \tag{26}$$

Substitute (25) and (26) in (22), and the resulting value of v_1' in (24). Then substitute the value of β from (20), and remembering that $M_1/M_2 = \gamma$ we obtain our final equation:

$$\tfrac{1}{2}\alpha_1(\gamma - 1) + \alpha_2\sqrt{\frac{\gamma T_2}{T_1}} = -\frac{\gamma n}{n+1}\sqrt{\frac{2\lambda}{3RT_1}}. \tag{27}$$

This equation furnishes us an approximate method of estimating the effect of various factors upon the reflection of atoms from a surface. This will best be illustrated by a few examples.

First Case: $m_1 = m_2$.

In the first place, let us consider the case of a substance in equilibrium with its own saturated vapor. We then have $T_1 = T_2$ and $m_1 = m_2$, so that $\gamma = 1$.

If we express λ and R in calories ($R = 2$). then equation (27) reduces to

$$\alpha_2 = -\frac{n}{n+1}\sqrt{\frac{\lambda}{3T}}. \tag{28}$$

This equation tells us how large α_2 must be in order that the atoms of vapor may be reflected. In the case of tungsten at 3000° K., $\lambda = 260{,}000$ calories, so that we have

$$\alpha_2 = -4.8\frac{n}{n+1}. \qquad (29)$$

The following table gives the values of α_2 corresponding to different values of n.

TABLE I

n	α_2	P
0	0	0.50
0.1	−0.435	0.23
0.2	−0.80	0.08
0.3	−1.10	0.028
0.4	−1.37	0.0087
0.5	−1.60	0.0028
0.6	−1.80	0.00093
0.7	−1.97	0.00032
1.0	−2.40	$17\text{x}10^{-6}$
2.0	−3.20	$14.0\text{x}10^{-9}$
3.0	−3.60	$1.0\text{x}10^{-9}$

In this table n gives the effective number of atoms which attract but do not subsequently repel the incident atom. We have seen that there is good reason to believe that the attraction is exerted by three, four, or even more atoms, while the repulsion is exerted principally by one or two. We may therefore expect the value of n to be of the order of 2 or 3. The above table shows, however, that even if n should be as small as 0.1, reflection of the incident atom can occur only if it collides with an atom for which $\alpha_2 = -0.445$, that is, an atom which is already moving by its thermal agitation with a velocity component away from the surface equal to 44 per cent. of the mean thermal velocity. The column headed P gives the probability, according to Maxwell's distribution law, that any given atom on a surface should have a velocity in a given direction exceeding $\alpha_2\bar{v}_2$. Thus, according to the table, only 23 per cent. of the atoms on the surface have an outward velocity component greater than 44 per cent. of the mean velocity. The probability P is calculated by the equation

$$P = \frac{1}{\sqrt{\pi}}\int_{\alpha_2\sqrt{3/2}}^{\infty} e^{-x^2}\,dx. \qquad (30)$$

With values of n as large as 2 or 3, the probability is negligibly small that an atom on the surface will have a sufficient velocity to cause the reflection of an incident atom.

The above calculations lead to the conclusion, which is in good accord with experimental facts, that the reflection of tungsten atoms from a tungsten surface takes place to a negligible degree only.

By equation (28) we see that the reflectivity of atoms from a surface will depend on the coefficient n and the ratio λ/T. It seems probable that n is of the same order of magnitude for all substances and has a value somewhere between 1 and 3. According to Trouton's rule the latent heats of evaporation of different substances are proportional to the absolute boiling points. Nernst finds that this rule is only approximate, and modifies it by placing the ratio λ/T proportional to log T. If we consider a series of different substances at "corresponding" temperatures the values of λ/T will not differ very greatly, but according to Nernst will be smaller the lower the absolute boiling point of the substance.

TABLE II

Substance.	T_0	λ	λ/T	α_2	P
H_2	20.4	205	10.1	0.92	.055
O_2	90.	1,680	18.7	1.25	.015
H_2O	373.	9,000	24.1	1.42	.0069
Hg	631.	12,300	19.5	1.28	.013
Pt	4200.	109,000	26.0	1.47	.0054
Mo	3900.	160,000	41.0	1.85	.0007
W	5100.	200,000	39.0	1.82	.00085

Table II contains data for a few substances. The absolute boiling point T_0 is given in the second column, while λ, the internal latent heat of evaporation at the boiling point, is given in the third. It is seen that the maximum range of the values of λ/T is only from 10 to 41, and, since this ratio in (28) occurs under the radical, the value of α_2 only varies within the ratio 1 to 2. The values of α_2 and P calculated by taking $n = 1$ are also given in Table II.

These data are calculated for the temperature of the boiling point. At lower temperatures α_2 would be larger so that P would be still smaller than the values given in the table.

In the above discussion we have derived a method of calculating the probability that an atom on the surface of a solid may have a sufficient velocity to cause an incident molecule to be reflected. The calculation was based, however, on the assumptions:

1. That the forces and motions involved are all normal to the surface.

2. That the collisions are perfectly elastic and that the work done on the incident particle by the attractive forces all appears as kinetic energy of this particle.

It is certain that the first assumption cannot correspond to the facts. The directions of motion of the incident particles after the collisions are probably distributed uniformly in all directions so that the chance of an atom being reflected is *very much* less than that given by P.

It is also probable that the second condition is not fulfilled, which must result in a still further decrease in the amount of reflectivity. Some idea of the rapidity with which adjacent atoms in a solid reach thermal equilibrium may be obtained from a consideration of the heat conductivity.

The problem is similar to that of a calculation of the "time of relaxation" for a gas. The distribution of velocities among the molecules of a gas in the steady state is given by Maxwell's distribution law. If a deviation from this law is brought about in some manner, and the gas is then left to itself, the distribution will rapidly return to that of Maxwell. The time required for the abnormal condition to subside is measured by the "time of relaxation," which Maxwell defines as the time needed for the deviation (measured in terms of kinetic energy) to fall to $1/e$th of its original value.

The following roughly approximate method will enable us to estimate the order of magnitude of the time of relaxation in a solid body.

Let us imagine that a single layer of atoms on the surface of a solid is at a temperature T, while the underlying layers of atoms are at zero temperature. If h is the heat conductivity of the solid, and σ is the distance between adjacent atoms, then the heat flowing between the first and second layers will be hT/σ per sq. cm. if we neglect the change in temperature of the second layer. The number of atoms in the surface layer will be $1/\sigma^2$ per sq. cm. and the heat capacity of each atom is $3k$, where k is the Boltzmann gas constant 1.37×10^{-16} erg./deg. We thus obtain

$$\frac{hT}{\sigma} = -\frac{3k}{\sigma^2} \cdot \frac{dT}{dt}, \tag{31}$$

or

$$ln \frac{T_0}{T} = \frac{h\sigma}{3k} t. \tag{32}$$

If we let T_0/T equal e, then t will become equal to the time of relaxation, which we may represent by t_r, thus

$$t_r = \frac{3k}{h\sigma}. \tag{33}$$

The times of relaxation for various substances as calculated by this equation are given in the fourth column of Table III. The data used in the calculation, h and σ, are given in the second and third columns. The values of σ were calculated from the density ρ and atomic weights A given in the fifth and sixth columns. For such substances as calcite and glass A was taken to represent the average atomic weight of all the atoms in the substance. The seventh column gives τ the natural period of oscillation of the atoms of the substance.

TABLE III

Substance.	h erg/cm. sec.	σ cm.	sec.	ρ g/cm³.	A	τ sec.	$\frac{t_r}{\tau}$
	$\times 10^7$	$\times 10^{-8}$	$\times 10^{-15}$			$\times 10^{-15}$	
Copper.......	3.84	2.3	0.46	8.9	64.	180	.0026
Tungsten.....	1.25	2.5	1.3	19.	184.	170	.0077
Platinum......	0.7	2.5	2.3	21.5	195.	210	.011
Mercury......	.082	2.9	17.	13.6	200.	640	.027
Quartz........	.09	2.3	20.	2.6	20.	186	.11
Rock salt.....	.06	2.8	25.	2.2	29.	250	.10
Calcite........	.034	2.3	53.	2.7	20.	138	.38
Soda-glass.....	.01	2.4	170.	2.5	21.	200	.85
Ice...........	.004	2.2	470.	0.9	6.	370	1.3
Sulfur........	.0026	2.9	550.	2.1	32.	460	1.2
Paraffin.......	.0025	2.0	790.	0.9	4.6	440	1.8

This natural period is the reciprocal of ν the atomic frequency (Eigenschwingungen). The atomic frequency may be calculated in any one of a half dozen different ways[31] with substantially similar results. The values given in the table have been obtained from the compressibilities K by means of Einstein's[32] equation

$$\tau \doteq \frac{1}{\nu} = 3.5 \times 10^{-8} A^{\frac{1}{3}} \rho^{\frac{1}{6}} K^{\frac{1}{2}}. \tag{34}$$

Objections may be raised against the use of this equation for the calculation of the periods of oscillations of the atoms of compounds, but it is not likely that the order of magnitude of the result will be in error. Koref[33] calculates by other methods that in a rock salt crystal the frequency of the sodium atom is 6.8×10^{12}, and that of the chlorine is 5.5×10^{12} The atomic frequency calculated from the value of τ in Table III is 4×10^{12}, which is not greatly different from Koref's results.

[31] Harkins and Hall., *Jour. Amer. Chem. Soc.*, *38*, 207, 1916.

[32] *Ann. Phys.*, *34*, 170, 1911.

[33] *Phys., Ztsch.*, *13*, 186, 1912.

The last column of the table gives the ratio of the time of relaxation to the natural period of oscillation of the atoms. In the case of the metallic substances this ratio is very much less than unity, which must mean that thermal equilibrium is established between adjacent atoms in a small fraction of the time necessary to complete a single oscillation.

Under these conditions it is apparent that our second assumption (elasticity in collisions) is not justified in the case of metals. It is probable, in fact, that atoms of metal vapor striking the surface reach practically perfect thermal equilibrium with adjacent atoms before they can possibly escape again from the surface. The amount of reflection during the condensation of metallic vapors is therefore probably extremely small. Since the high heat conductivity of metals is related to their electrical conductivity, we may conclude that "free electrons" play an important part in the mechanism of the condensation of metallic vapors.

From Table III we see that even in the substances of low heat conductivity such as ice or sulfur, the "rate of relaxation" is so high that the collisions must be far from elastic. A slight loss of energy to adjacent atoms, must have a very great effect in decreasing the chance that an incident atom or molecule will be able to escape, so that even with nonmetallic substances it is probable that the reflection of molecules occurs to a much smaller degree than would be estimated from the values of P given in Table II.

However, it would not be safe to conclude that in all cases where molecules strike similar molecules (or atoms) on a surface that the reflectivity must be negligibly small. We have seen that there is evidence that metals in contact with hydrogen even at low pressures have their surface completely covered with a layer of hydrogen atoms or molecules. The accommodation coefficient 0.25 observed for hydrogen in contact with platinum, indicates that a considerable fraction of the hydrogen molecules striking other hydrogen atoms or molecules on the surface is reflected. The reasons for the high reflectivity in this case probably are:

1. The heat of condensation λ is very small. By Table II we see that λ for liquid hydrogen at its boiling point is only 205 calories per gram molecule. It is probable, however, that the hydrogen atoms on a metal surface are held by very strong chemical forces [34] so that they are much more thoroughly saturated than the atoms or molecules in liquid hydrogen. There is good reason to think, therefore, that such a layer of hydrogen atoms would exert only very weak attractive forces on incident hydrogen molecules, and that the value of λ for the condensation of the second layer would be much less than 205 calories.

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[34] There is reason to think that for the condensation of the first layer of atoms of hydrogen on platinum the value of λ is about 40,000 calories per gram molecule.

We see by equation (28) that a small value of λ would tend to increase the number of atoms reflected.

2. The temperature is very high compared to the boiling point of hydrogen, and this fact, according to (28) and (30), would tend to increase the chance of reflection. It may also decrease λ. Although the heat of evaporation of liquids decreases to zero when the critical temperature is reached, we must not consider that λ also disappears at this temperature. In the sense in which we are using this quantity it represents the work done in separating the atoms of the solid or liquid to an infinite distance from each other. This quantity evidently may have considerable values even at temperatures much above the critical temperature.

3. The atoms forming the adsorbed layer on the surface may be so rigidly held by the underlying metal as to greatly increase the tendency for the weakly attracted incident atoms to be reflected. In deriving equation 28 it was assumed that during the time of a collision, the atom on the surface is free to move according to the usual laws of elastic collisions. If the adsorbed atoms are rigidly held to the metal atoms the effective mass of the adsorbed atoms would be greatly increased. According to equation (27), this would tend to increase the reflectivity.

Another effect produced by the close coupling of the adsorbed atoms to the metal and the loose coupling to the incident atoms is to lengthen the time of relaxation of the incident atoms.

Second Case. Unlike Atoms.—So far, we have considered the condensation of a vapor on a solid whose surface consists of the same kind of atoms. If atoms of a light gas strike the surface of a solid consisting of heavy molecules, the case becomes more complicated, since we must use equation (27) instead of (28). Let us consider the case of hydrogen molecules striking an absolutely clean surface of tungsten or other heavy metal. For such a case we may put approximately $\gamma = .01$, so that, if we place $T_2 = T_1 = T$ and $R = 2$, equation (27) becomes

$$\alpha_2 - 4.95\,\alpha_1 = -\,0.058\frac{n}{n+1}\sqrt{\frac{\lambda}{T}}. \tag{35}$$

From this equation we may estimate the amount of reflection which would occur if the directions of all motions and forces were normal to the surface. Under actual conditions the amount of reflection would be considerably smaller. In making this calculation we substitute in (35) the value of n, γ, and T and then choose particular values of α_1, and find α_2 by the equation. Thus if we place $n = 1$ and $\gamma = 40{,}000$, we find the pairs of values of α_1 and α_2 given in the first two columns of Table IV.

The value of α_2 gives the maximum (positive) velocity which an atom of the solid may have and still cause the reflection of an atom colliding

TABLE IV

α_1	α_2	P_1	P_2
+0.	−0.34	1.00	0.28
+0.1	+0.15	0.98	0.60
0.2	+0.65	0.94	0.87
0.3	+1.14	0.87	0.98
0.4	+1.64	0.79	1.00
0.5	+2.14	0.69	1.00
1.0	+4.61	0.22	1.00

with it. Thus from the table we see that if a molecule of hydrogen (A) starts from rest ($\alpha_1 = 0$) and is attracted towards the metal surface, it will only be reflected if the metal atom which it strikes is moving *towards* it with a velocity numerically in excess of that corresponding to $\alpha_2 = 0.34$. If, however, the hydrogen molecule starts with an initial velocity (normal to the surface) corresponding to $\alpha_1 = 0.1$ we see that it may be reflected even if it strikes a metal atom moving *away* from it with a velocity as large as that corresponding to $\alpha_2 = 0.15$.

The probability that a molecule striking the surface should have a velocity greater than α_1 is given by

$$P_1 = e^{-\frac{3}{2}\alpha_1^2}. \tag{36}$$

On the other hand, the probability P_2 that a molecule on the surface should have a velocity component less than that corresponding to α_2 may be readily calculated by means of equation (30). The probabilities P_1 and P_2 have been entered in Table IV. From these data we see for example, that 87 per cent. of all the incident molecules have velocities towards the surface greater than that corresponding to $\alpha_1 = 0.3$. In order that these molecules may be reflected it is necessary that α_2 shall not exceed 1.14, but according to the fourth column we see that 98 per cent. of the metal atoms have a value of α_2 less than 1.14.

From these data by approximate integration of $\int P_2 dP_1$, it can be shown that of all molecules striking the surface 97.3 per cent, would be reflected if we could assume all motions and forces to have directions normal to the surface. This figure gives us an upper limit for the amount of reflection. This result is not greatly different if we take other values for λ or n. Thus if we take λ or n (or both) equal to zero, we obtain in a similar manner to that used above, the value 98.7 per cent. for the maximum possible reflectivity. On the other hand if we take $n = \infty$ and $\lambda = 40{,}000$ we find 95.1 per cent.

In many chemical and physical problems it is important to know how closely the reflectivity can approach 100 per cent. Thus in calculating the vapor pressure from the rate of evaporation, we made use of $(1 - r)$. (See equation (1).) In this case, where $\gamma = 1$, we have seen that we may always place $r = 0$. Similarly in estimating the velocity of a chemical reaction we may use an equation similar to (1) in which we use ε in place of $(1 - r)$.

In studying the mechanism of such reactions we need to know the order of magnitude of $1 - r$. Thus suppose in a given case we find that only one molecule reacts out of every thousand striking the surfaces, that is $\varepsilon = 0.001$. In interpreting this result we need to know whether it is possible that 99.9 per cent. of the molecules are actually reflected.

From the calculations given above, it appears that the reflectivity can in no case exceed 99 per cent., and must in all probability be much less than this. Therefore a value of ε as small as .001 must be accounted for in some other way than by reflectivity, as for example by assuming that the greater part of the surface is covered with a material on which the given reaction does not take place.

The smallest accommodation coefficient that has been observed is 0.19 (hydrogen). This corresponds according to Baule's theory (equation 8), to a reflectivity of about 83 per cent., a value which is in reasonable agreement with the upper limit of 95–99 per cent. calculated above.

It thus seems extremely probable that when gas molecules strike solid bodies in no case are more than 90 per cent. of the molecules reflected.

Chapter Sixteen

THE EVAPORATION OF ATOMS, IONS, AND ELECTRONS FROM CAESIUM FILMS ON TUNGSTEN *

PRECISION METHODS FOR measuring the number of caesium atoms adsorbed on tungsten are described. With these methods for determining θ (the fraction of the tungsten surface covered with Cs), the rates of atom, ion and electron emission are measured as functions of θ and T, the filament temperature. *The rate of atom evaporation,* ν_a, increases rapidly with θ and with T. At low filament temperatures and high pressures of Cs vapor the concentration of adsorbed Cs atoms approaches a limit 3.563×10^{14} atoms cm^{-2} of true filament surface (one Cs atom for four tungsten atoms). This film ($\theta = 1$) exhibits all the characteristics of a true monatomic layer. The formation of a second layer begins only at filament temperatures corresponding to nearly saturated Cs vapor. A theory of the formation of a second and of polyatomic layers is given and experiments supporting it are described. *The heat of evaporation* (given by the Clapeyron equation) for Cs atoms from clean tungsten is 2.83 volts (65,140 calories), 1.93 volts or 44,473 calories at $\theta = 0.67$, and 1.77 volts or 40,757 calories at $\theta \simeq 1$. The adsorbing tungsten surface after proper aging is homogeneous, except that about 0.5 per cent of it (active spots) can hold Cs more firmly than the rest. The procedure in obtaining *electron* (ν_e) and *ion* (ν_p) *emission* for zero field and the large changes in the effect of external field with θ are described. From both ν_e and ν_p the contact potential V_c is calculated, agreeing, except for very concentrated films, with V_c calculated entirely from data on neutral atom evaporation. At constant temperature the electron emission increases to a maximum at $\theta = 0.67$ and decreases as $\theta = 1$ is approached. The positive ion emission increases rapidly to a maximum at $\theta \simeq 0.01$ and then decreases. The work function (exponent in Dushman type equation) for electrons at $\theta = 0.67$ is 1.70 volts (clean tungsten $= 4.62$ volts). The work function for ions is 1.91 volts at $\theta = 0$, and 3.93 volts at $\theta = 0.67$. It is shown by experiment that the saturated ion current from a clean hot (1200–1500° K.) tungsten filament is an

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* In collaboration with John Bradshaw Taylor.

accurate measure (experimental error of about 0.2 per cent) of the number of atoms striking the filament per second. *The condensation coefficient* (α) for atoms striking a tungsten filament is proved by experiment to be unity from $\theta = 0$ to nearly 1. The important bearing of this fact and of the experimentally observed existence of *surface migration* or diffusion on the *mechanism of evaporation and condensation* in dilute and concentrated films is discussed. In addition surface migration is correlated with irregular ion evaporation rates occurring when two phases (dilute and concentrated films of Cs) exist on the tungsten surface. *Transient effects* in which θ changes with time are studied and entirely explained by the observed rates of evaporation and condensation. This and other facts are used to justify a *surface phase postulate* according to which all the properties of the adsorbed film are uniquely determined by θ and T.

I. INTRODUCTION

Caesium films on tungsten form an important and interesting case of adsorption. The adsorbed atoms are held on the tungsten by such large forces that remarkable changes in the thermionic properties of the tungsten can be observed. As the tungsten surface can be completely cleaned and the supply of caesium atoms can be controlled, this system is capable of furnishing quantitative information regarding adsorption and the electrical properties of surface films.

Films of alkali metal atoms on tungsten have been the subject of several investigations. Langmuir and Kingdon[1] found that caesium atoms adsorbed on tungsten greatly increased the electron emission of the tungsten and showed that caesium atoms striking a hot clean tungsten filament were converted into positive ions which could be collected by a plate at a negative potential. Both the electron and ion emissions were functions of the temperature (T) of the filament and of the fraction (θ) of the surface covered with caesium. The electron emission increased to a maximum at a certain value of θ and decreased with further increase in θ. The positive ion emission became appreciable only for low values of θ; at higher values of θ, caesium films evaporated only as neutral atoms. Only rough estimates of θ were made in this work.

Recently Langmuir[2] has treated the properties of caesium adsorbed on tungsten in a general discussion of evaporation, condensation, and adsorption, and has given a partial derivation of equations used in this paper.

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[1] I. Langmuir and K. H. Kingdon, *Science, 57,* 58 (1923); *Proc. Roy. Soc., A107,* 61 (1925).

[2] I. Langmuir, *Jour. Amer. Chem. Soc., 54,* 2798 (1932).

Becker[3] has studied the evaporation of atoms, ions, and electrons from caesium films on tungsten and made measurements of θ. He attributed the maximum electron emission to a single complete layer of caesium atoms and the subsequent decrease in emission to the formation of a second layer of caesium atoms.

The present investigation was undertaken for the purpose of determining quantitatively the dependence of the rates of neutral atom evaporation (ν_a), ion emission (ν_p), and electron emission (ν_e) on θ, filament temperature T, and the field strength; ν_a, ν_p and ν_e represent the number of atoms, ions, or electrons evaporating per unit area, per unit time. To facilitate correlation of ν_p and ν_e with θ, the greater part of the work has consisted in establishing θ as a function of caesium pressure and filament temperature.

In the steady state,

$$\alpha\mu_a = \nu_a; \qquad (1)$$

that is, the number of atoms evaporating per unit area per unit time (ν_a) is equal to the number condensing, which is equal to the number arriving per unit area per unit time (μ_a), multiplied by the condensation coefficient α. Evidence regarding the nature of α will be given (Section XI) and it will be shown that under our experimental conditions α is equal to unity. Therefore the experiments which give θ as a function of μ_a also give ν_a as a function of θ.

Let us now postulate that ν_a, ν_p and ν_e are functions of θ and T only. The distribution of atoms is assumed to be uniform and independent of the way (e.g., by evaporation or condensation) in which θ was reached. This "surface phase postulate" will be discussed and justified in Section XI. Determinations of ν_e and ν_p at various pressures then enable us to express ν_e and ν_p as functions of θ and T.

II. APPARENT AND TRUE FILAMENT SURFACE AND DEFINITION OF θ

The apparent area S_A of the filament surface is that calculated from the dimensions of the filament (πld). Actually after heating to 2900° during aging, a tungsten filament becomes etched and develops[4] dodecahedral crystal faces (110) in which there are 1.425×10^{15} tungsten atoms per cm^2. The actual surface area S is thus greater than S_A (see Fig. 1).

It so happens that crystals of metallic caesium[5] have the same type of lattice (body-centered cubic) as tungsten and the lattice constant (6.17A) is almost exactly double that of tungsten (3.15A). Thus if, in a complete monatomic film of caesium on tungsten, the caesium atoms arrange themselves in a surface lattice identical with that of the tungsten surface but with double spacing, there will be one caesium atom for every four tungsten atoms, all the adatoms will be similarly placed with respect to the underlying tungsten atoms, and the adatoms will be at the same distances from one another as in metallic caesium.

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[3] J. A. Becker, *Phys. Rev., 28,* 341 (1926); *Jour. Amer. Electrochem. Soc., 55,* 153 (1929).

[4] I. Langmuir, *Phys. Rev., 22,* 374 (1923).

[5] Simon and Vohsen, *Zeits. f. physik. Chemie, 133,* 165 (1928).

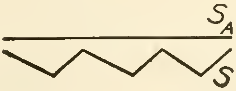

Fig. 1. True (S) and apparent (S_A) filament surface.

Because the strong forces between the caesium and the tungsten atoms must tend to make the adatoms occupy definite elementary spaces[6] determined by the tungsten lattice, we believe we are justified in adopting this 4 to 1 relation as a postulate in our further investigations. We may therefore put for the true surface concentration σ_1 of a complete caesium film on tungsten

$$\sigma_1 = 3.563 \times 10^{14} \text{ atoms cm}^{-2}. \tag{2}$$

Experiments which will be described in Section V and XII have shown that with the particular filament used, the apparent surface concentration σ_{A1} for a complete film of caesium on tungsten is

$$\sigma_{A1} = 4.80 \times 10^{14} \text{ atoms cm}^{-2}. \tag{3}$$

The ratio σ_{A1}/σ_1, which is 1.347, is thus equal to S/S_A, the ratio of the true to the apparent filament surface. Tonks has calculated[7] that with a random distribution of dodecahedral crystals the *minimum value* of S/S_A is 1.225, a value which supports our postulate.

We intend to test this postulate in future work by comparing values of σ_{A1} obtained with adsorbed films of caesium, rubidium and potassium on a single tungsten surface. If the value σ_1 as given above is correct, we should expect that σ_{A1} will be the same for all alkali metals.

Let σ_A be the apparent surface concentration of adatoms obtained by dividing the total number of adatoms by S_A, the apparent surface area (πld). Then the true surface concentration σ is $\sigma_A S_A/S$. It is probable that S/S_A may vary somewhat for different filaments according to the aging treatment and the fineness and orientation of the crystals. The intrinsic properties of the adsorbed film are presumably dependent on σ rather than

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[6] I. Langmuir, *Jour. Amer. Chem. Soc., 38,* 2287 (1916); *40,* 1366 (1918).
[7] L. Tonks, *Phys. Rev., 38,* 1030 (1931).

σ_A. Since, however, our knowledge of σ depends upon our postulated value of σ_1, as given by Eq. (2), it is preferable to express these properties as functions of the covering fraction θ defined by

$$\theta = \sigma_A/\sigma_{A1}. \tag{4}$$

All the values of θ in this paper have been calculated in this way from σ_A by using the value of σ_{A1} given by Eq. (3). It should be noted that θ is also equal to σ/σ_1.

We must also have clearly in mind the relation of S and S_A to our definitions of μ and ν. We shall define μ_a as the number of incident atoms per unit time per unit area of *apparent surface* S_A. Thus from the kinetic theory

$$\mu_a = p(2\pi mkT)^{-\frac{1}{2}} = 3.796pT^{-\frac{1}{2}} \text{ atoms cm}^{-2}\text{ sec.}^{-1} \tag{5}$$

where p is the pressure in baryes and T is the temperature of the caesium vapor.

In a similar way we define ν_a as the number of atoms which escape from the filament by evaporation per unit time per unit area of *apparent surface* (S_A).

We wish, however, to know the rate of evaporation per unit area of true surface S for this alone should be an intrinsic property of the adsorbed film.

In the steady state to which Eq. (1) applies, the condensation on and evaporation from each element of area must balance. The atomic flux density in the neighborhood of the filament must therefore be isotropic just as is the heat radiation within an enclosure at uniform temperature. The values of μ and ν over the surface of S, in Fig. 1, must thus be the same as over the surface S_A.

Consider now the irreversible evaporation of adatoms from a filament in a space in which $\mu = 0$. We see from S in Fig. 1 that a large fraction of the atoms that evaporate from the valleys (and a smaller fraction from the peaks) are intercepted by the surface of the opposing peaks before they can escape. The concentration of adatoms thus decreases near the peaks faster than in the valleys unless surface mobility equalizes their concentration.

If mobility does maintain a uniform θ and if $\alpha = 1$ so that all incident atoms condense, it follows from the reversibility principle (see Section XII) that the emission occurs in accord with Lambert's cosine law. The situation is exactly analogous to that in optics where the brightness of an incandescent black body is independent of its contour.

During irreversible condensation from a vapor with a given μ, the concentration at the peaks should increase faster than in the valleys, assuming no mobility. Since the experiments (see Section XI) have shown no difference in properties of a film with a given average value of θ whether it was obtained by irreversible condensation or evaporation, we must conclude that surface mobility equalized θ over the surface. Because of this mobility and the fact that $\alpha = 1$, we may therefore conclude that the values of ν defined in terms of apparent surface are identical with the evaporation rates per unit area of true surface.

III. METHODS FOR DETERMINING θ

There are four methods available for determining θ. Common to all methods is the measurement of the caesium vapor pressure (controlled by bulb temperature) in terms of μ_a, by observing the positive ion current to a collector at a negative potential with respect to a hot ($>1200°$ K.) tungsten filament. As will be demonstrated later, every atom striking the filament leaves as a positive ion so that I_p/e, the saturation positive ion current density divided by the electronic charge, gives μ_a.

Becker's method

Becker observed the time (t_m) required for the electron emission from a filament (initially cleaned by flashing) to reach a maximum value while the filament at temperature T_1 was being coated by a constant supply of Cs vapor. At the maximum, θ was assumed to be unity, that is, the film was taken to be a complete monatomic layer. It was then possible to raise the temperature of the filament to various temperatures (T_2), where the equilibrium θ was less than unity. If the temperature was now lowered to T_1, the electron emission again passed through a maximum as θ increased through unity. The time (t_3) needed for this completion of the film served to measure the θ at T_2 since $\theta = 1 - t_3/t_m$.

Direct flashing method

If a tungsten filament having a film for which θ is less than 0.08 is suddenly flashed in an accelerating field at a high temperature, all the caesium evaporates as ions giving a ballistic kick on a galvanometer. The filament area together with the ballistic calibration of the galvanometer allow calculation of σ_A and hence of θ.

Two filament method

As shown diagrammatically in Fig. 2, two parallel straight tungsten filaments, A and B, were mounted near the axis of three coaxial cylindrical electrodes c_1, c_0 and c_2, placed end to end so that by the guard-ring principle the electron or ion emissions from a known length of the central part of either filament could be measured. The tube is highly evacuated but contains saturated caesium vapor whose pressure is controlled by the tube temperature. The rate of arrival of atoms, μ_a, is measured with B at a temperature of ∽ 1200° K. This steady current is then balanced out so that only changes in current are indicated by the galvanometer (G) connected to c_0; c_1, c_2 and c_0 were usually maintained at 45 volts negative to filament B. The potential of filament A is made 41 ± 2 volts negative to B (4 ± 2 volts positive to c_1, c_2 and c_0). Filament A is then cleaned by flashing at 2400° K. After a steady state (θ) is reached on its surface at any of a series of lower temperatures (300 — 1200° K.), the temperature of A is suddenly raised to about 1800° so that at these voltages all the adsorbed atoms evaporate instantly as neutral atoms, which travel in straight lines towards the cylinders c. A definite fraction f of these, however, are intercepted by the hot filament B and are converted into ions which pass to the cylinder c_0. The resulting ballistic kick indicated by the galvanometer, together with the known diameters of A and B and the distance of A from B give data for the calculation of σ_A and θ.

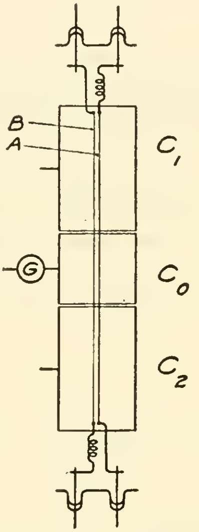


Fig. 2. Filament and collector arrangement in two filament method (diagrammatic).

The use of the second filament B as a means of measuring concentrations on filament A too high to be flashed directly from A as ions was suggested by Dr. Tonks of this laboratory.

The potential chosen for filament A insures that neither ions nor electrons shall pass to c_0 as the adsorbed atoms are suddenly evaporated.

The correct potential for A is most easily found by flashing A when nearly fully coated, with B cold. If A has been made too negative with respect to c_0, a ballistic kick due to electrons is observed; if not sufficiently negative a kick due to ions is noted. With the correct adjustment (critical only to about ± 2 volts) there is no detectable galvanometer deflection when A is flashed even if the initial values of θ on A are varied from 0 to above 1. This fact that the potential of A can be varied as much as 4 volts without detectable galvanometer deflections when B is cold proves that the zero value of current is not due to a balance between electron and ion currents from A, but that each of these currents is zero. This is undoubtedly caused by space charge limitation of the currents during the excessively short time that they can flow while the filament is being flashed. We therefore believe that no source of error is introduced into these measurements by currents from A. Although the sudden evaporation of atoms was usually accomplished by heating the filament by a condenser discharge, increasing the filament current to a value giving a temperature of about 1800° by closing a switch in a battery circuit also gives sufficiently rapid evaporation.

The accumulation method

If μ_a is small, changes in the properties of the film with time can be measured as θ increases slowly from zero. In this method ν_a must remain equal to zero since σ_A and θ are found from the product $\mu_a \times t$. This is accomplished either by working in the lower ranges of θ or at low filament temperatures.

Comparison of the methods for determining θ

(a) Becker's method may be used to determine θ's from about 0.01 to the optimum value θ_{opt} which gives the maximum in the electron emission; it will be shown later that $\theta_{\text{opt}} = 0.67$. The method requires not only that θ_{opt} shall be attained and that the electron emission at the optimum be measurable, but also that reevaporation of atoms is negligible until the maximum is passed. Thus with the sensitive galvanometer used in the present experiments (7×10^{-11} amp./mm) the allowable μ_a was limited to the range between approximately 6×10^{11} and 2×10^{13}, using a testing temperature (T_1) of $\sim 550°$ K. At lower testing temperatures the electron emission cannot be measured. A higher testing temperature raises the lower limit for μ_a. Even though θ_{opt} may be passed through, unless the testing temperature is low enough, atom evaporation may begin near θ_{opt} causing an increase in the time (t_3) required to reach θ_{opt} and a consequent error in the determination of θ. At higher values of μ_a the coating time becomes too short in comparison with the times required to bring the filament from a high temperature to a steady state at the lower testing temperature. For example, a 2 mil filament requires $\sim$ 15 seconds to cool from 1220° K. to 600° K. A filament in a bulb containing caesium at room temperature is completely coated in less than one second. The method also fails at high pressures because the θ's to be measured may already be above the optimum.

We have often found another serious difficulty in the application of Becker's method. Fig. 3 shows emission *vs.* time curves taken as in Becker's method. The curve *a* with a single maximum is obtained for caesium on a clean homogeneous tungsten surface. With extremely minute traces of gaseous impurities which are sometimes hard to avoid but which do not interfere with the application of the other methods of determining θ, we have often obtained two maxima as shown in curve *b*. With slight modification of the conditions the two maxima may merge into one. In such cases difficulties of interpreting the curves may lead to considerable error in the determination of θ.

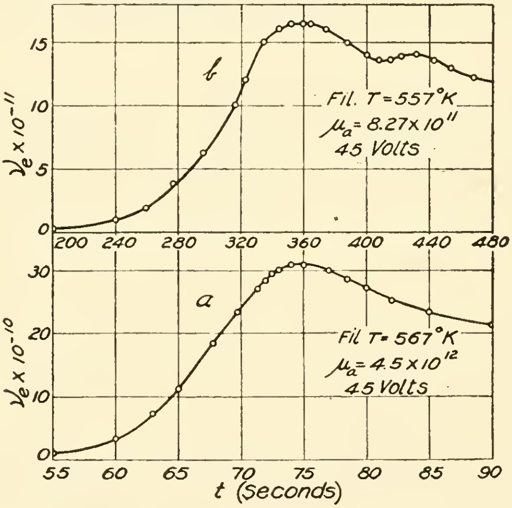


FIG. 3. Electron emission *vs.* time curves as obtained in Becker's method for measuring θ. (a) Clean filament, (b) partly gas covered.

(b) The direct flashing method is applied only below $\theta \sim 0.08$ but is so extremely sensitive that θ as low as 10^{-4} can be measured easily.

(c) The accumulation method may be used to produce any value of θ provided μ_a is kept below $\sim 10^{13}$ to give sufficient time for observations. It should find a useful application in the study of contact potentials. Known changes in the surface condition of an electrode receiving electrons can be produced. The resultant changes in contact potential could then be measured up to $\theta = 1$. If the filament or electrode can be cooled sufficiently below the temperature of the tube, the properties of polyatomic films may be studied.

(d) The two filament method was used in the present investigation to study θ from 0.05 to unity. It may be used to study even polyatomic films which may be formed by maintaining the filament for a short time in saturated Cs vapor or by producing supersaturated vapor by rapidly heating the bulb after the filament has cooled.

Calibrations

The validity and accuracy of the various methods for determining θ were tested chiefly by observation of transient effects, i.e., phenomena involving changes in θ with time. In these tests it was assumed first that α is unity under all experimental conditions and second that the positive ion current from a clean hot tungsten filament is an exact measure of μ_a. Experimental proof of both assumptions will be given in Section XI.

If a clean tungsten filament is allowed to coat with caesium for the time t in a retarding field for ions ($V_p = 0$), the direct flashing method, if valid, should give measurements from which the number of atoms accumulating per cm² in the time t can be calculated. This number should be $\mu_a \times t$.

Fig. 4 shows data obtained by the direct flashing method with the filament at room temperature during the accumulation period. The ordinates are σ_A (atoms cm^{-2}) as calculated from the ballistic galvanometer kicks. If Q is the quantity of electricity corresponding to the observed kick, $\sigma_A = Q/S_A e$ atoms cm^{-2}, where e is the electron charge. The galvanometer was calibrated ballistically by discharge of a standard condenser charged to a known voltage. The sensitivity was 3.3×10^{-10} coulombs mm^{-1}. The

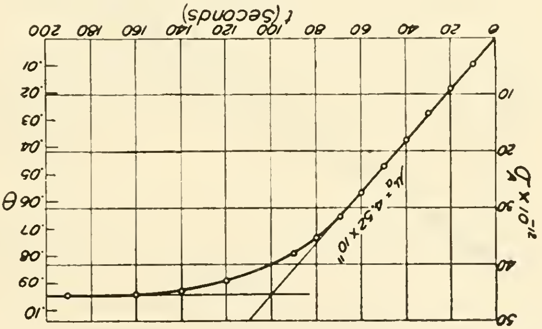


FIG. 4. Accumulation of caesium (concentration σ_A) with time as obtained by the direct flashing method. Filament at room temperature.

right-hand ordinates are the values of θ. Each point shown corresponds to a separate run in which Cs was allowed to accumulate for the time t after cleaning the filament by flashing.

The straight line in the figure has been drawn with the slope μ_a as given by the steady ion current. The points lie on this line within the experimental error of <1 percent for θ below about 0.07. The deviation above $\theta = 0.07$ is due to evaporation of Cs partly as atoms during the flash to obtain the ballistic kick. These curves remained unchanged if the coating temperature was varied from 300° to 800°. At still higher temperatures, deviations set in due to the reevaporation of arriving Cs atoms. These will be described in Section XI.

In the same way the 2-filament method was tested by measuring accumulated amounts of caesium corresponding to θ from ~ 0.05 to nearly 1.0. In this case the ballistic kick Q should equal $S_A \mu_a t f e$, where f is the fraction of the atoms intercepted by filament B. As found from the distance (2.85 mm) between filaments A and B, measured by a microscope with eyepiece scale, f was 0.0071. On plotting the observed values of σ_A, calculated from the ballistic kicks, $(\sigma_A = Q/S_A e f)$, it is seen, Fig. 5, that these values have accurately the calculated slope, μ_a, but are displaced slightly with respect to the calculated line. Thus the kicks extrapolated to zero time were not zero. This displacement was shown to be independent of θ and caesium pressure. A brief investigation did not reveal the cause of the displacement; it is probably connected with the pressure lags mentioned in the next section. This small empirical correction (−0.0086) was applied to all values of θ obtained by the 2-filament method.

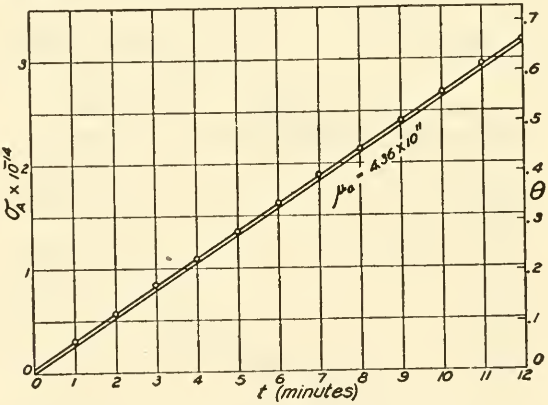


FIG. 5. Calibration of two filament method.

In addition to these preliminary comparisons, later measurements of equilibrium values of θ by both the direct flashing and 2-filament methods in the range of θ from 0.05 to 0.08 were in good agreement.

Becker's method was tried out extensively and the limitations already given as to testing temperature and Cs pressure found.

IV. DESCRIPTION OF THE EXPERIMENTAL TUBE

To obtain accurate results by the foregoing methods many precautions are necessary in the construction of the apparatus and in its use.

The caesium pressure must be exactly controlled. The ordinary construction with metal cylindrical electrodes inside a glass bulb does not allow this. These cylinders become heavily coated in the presence of caesium vapor and since their temperature is indefinite and affected by radiation from the filaments, the rate of supply of Cs is non-uniform. The use of metal electrodes deposited directly on the walls of the tube avoids this, by giving more direct thermal contact with the bath liquid.

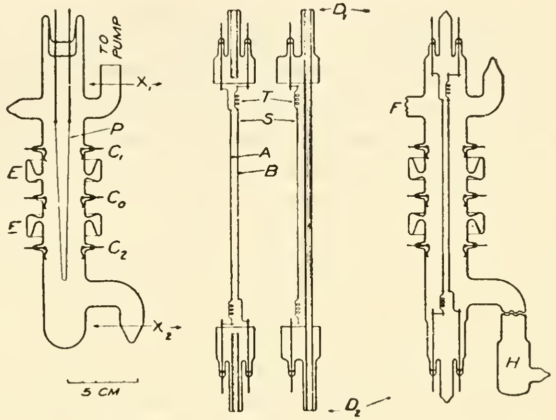
The guard ring principle must be employed to allow measurement of currents from a known length of filament and to prevent measurement of currents from the ends or any portion of the filament which is not at the temperature of the central part of the filament. This is far more important in studies of caesium on tungsten than for clean tungsten. For example, if the central part of the filament is hot enough to be practically free from caesium, the end portions may be cooled sufficiently by the leads to have high values of θ from which the electron emission is thousands of times greater than from the cleaner central part.

The filaments should be so long that the cooling effect of the leads does not cause a non-uniform temperature over the central part even at low filament temperature.

(1) *Preparation of the tube*

Fig. 6a shows the glass mantle. The two annular folds (E) were made by pressing together while hot two enlarged sections of the tube. These folds divide the tube into three sections, c_1, c_0 and c_2, spaced ~½ mm apart, which later are to serve as electrodes. The connections to each electrode consist of tungsten seals from which 5 mil platinum wires are led to and are partially imbedded in the glass wall.

In Fig. 6a, P is the 10 mil platinum filament in place ready for the coating of the walls by evaporation. The tube at this stage was evacuated and baked at 400° C. for 2 hours, after which the oven temperature was lowered to about 300° C. The filament was now heated to a temperature where the evaporation of platinum in a period of about two hours was sufficient to coat the glass walls with a film whose resistance as measured between the pairs of leads to each section was less than 50 ohms. Since the greater part of each annular fold received no platinum in this evaporation process, these folds now acted as insulation between the three electrodes, c_1, c_0 and c_2. In addition these folds could later be conveniently heated by a few turns of resistance wire to prevent electrical leaks which otherwise often occurred at the higher caesium pressures.



(a) (b) (c) (d)

Fig. 6. Preparation of the experimental tube. (a) Outer glass mantle with platinum filament for coating walls. (b) Frame on which the filament structure is mounted and inserted in outer tube. (c) Frame turned through 90°. (d) The completed tube.

(2) *Preparation of the filament structure*

Since the filaments A (2 mil) and B (5 mil) must be accurately and uniformly spaced, they were first mounted on a frame as shown in Fig. 6b. This frame consisted of two pairs of glass seals (with tungsten leads) separated by a rigid glass rod. Fig. 6c shows the frame turned through 90°. The filament structure was adjusted and aligned entirely on this frame. The total length of each filament was 30 cm while the length of the central part in cylinder c_0, was 3 cm. To obtain this length of 30 cm more conveniently, the ends of each filament were wound into tight spirals, (S), the 2 mil filament being wound on a 3 mil mandrel and the 5 mil on a 5 mil mandrel, leaving a straight length of 10 cm between the spirals. By trial the tension springs (T) were selected and stretched so that when heated the filaments remained taut and did not shift laterally.

(3) *Complete assembly*

Now the platinum coating filament was removed at X_1 and the tube also opened at X_2. The frame carrying the filaments was next inserted, lower end (of smaller diameter then the inside of the main tube) first. It was sealed at X_1 and X_2 after which the glass rod having fulfilled its purpose was removed and its supporting tubes sealed off at D_1 and D_2. The filaments remained as previously adjusted. Fig. 6d shows the completed tube. The tube, with charcoal tube and ionization gauge attached at F, was then evacuated, rebaked and tested with the gauge for leaks and slow evolution of gas. The charcoal tube was separately outgassed at a higher temperature. Just before sealing off, a thin walled glass capsule of caesium was broken in a side tube and about one cc of caesium distilled into the large appendix H. The usual gas evolution in this process was avoided by using capsules filled with caesium which had already been well freed from gas.

The filaments A and B were 2.85 mm apart as determined by examination with a microscope through the clear glass annular folds. From this spacing and the known diameters of A and B, the fraction (f) of the atoms leaving A which are intercepted by B was calculated. $f = 0.0071$.

Aging of tungsten filaments

In previous work on the electron emission from clean tungsten it has been found necessary to age the filaments to obtain reproducible results. With Cs on W an aging process is perhaps even more important. All filaments used were aged at 2400° K. for at least 10 hours followed by an hour at 2600° and finally several short flashes at 2900°. It was further shown that the rate of evaporation of Cs ions from the filament was a most sensitive guide in this process. The cold filament was allowed to coat with Cs, the tube being at room temperature. The tube was then immersed in liquid air to freeze out all Cs vapor. Next the filament was heated to a temperature (about 850° K.) where the rate of ion evaporation was slow enough to be followed on a sensitive galvanometer. If the filament were not sufficiently aged, the plot of evaporation rate against time or against the amount of Cs, θ, left on the surface at any time, showed a number of maxima or peaks as in Fig. 7. These peaks were also observed by Kingdon in earlier unpublished work. Such irregular evaporation is probably caused by non-uniformities of the tungsten surface and would make it difficult to obtain rates and heats of evaporation characteristic of the whole surface. After sufficient aging, the rates of evaporation increase to maximum values and the peaks merge into a smooth curve as also shown in Fig. 7. Further aging produces no change. It was found that a fine grained filament was most easily brought into this final condition and such filaments were used in this work. The average grain size in these filaments was about one-fifth the diameter of the wire.

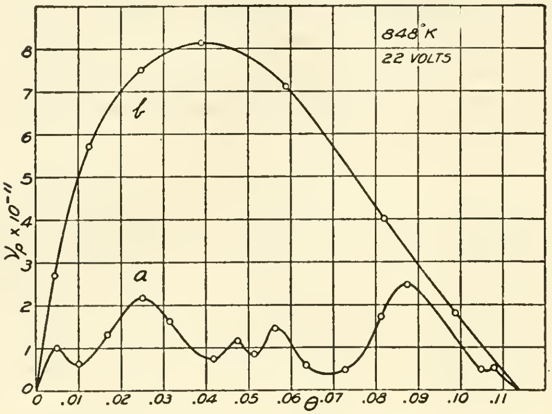


FIG. 7. (a) Irregular evaporation rate for ions from an unaged filament. (b) Uniform variation of evaporation rate from a sufficiently aged filament.

Control of μ_a

In these experiments μ_a was varied about one thousand-fold from $\sim 10^{11}$ to 10^{14} atoms cm^{-2} sec.$^{-1}$. To maintain any particular pressure a large Dewar flask containing kerosene vigorously stirred surrounded the tube. The bath was heated electrically or cooled below room temperature by use of a coil containing liquid air. In preliminary experiments only the appendix *H* was immersed in the bath, the rest of the tube being at room temperature. It was then observed that the galvanometer readings following ballistic kicks, especially at high θ's, did not return immediately to zero, but showed a lag of several seconds. This lag was found to be due to the burst of atoms suddenly liberated from filament *A*. These apparently did not come instantly to equilibrium with the walls of the tube and there resulted a pressure increase of short duration which was registered on filament *B*. This effect was eliminated by freshly coating the walls of the tube with caesium before any daily series of experiments and by immersing the whole tube in the bath liquid. This served to cover and keep covered any spots on the walls of the tube which were not acting as true caesium surfaces.

Filament temperatures

The filament temperatures were found from the known diameter and the measured value of filament current. The temperature scale for tungsten and the tables given by Jones and Langmuir [8] were used.

Below $\sim$ 550°, even with the long filament used, cooling of the central part of the filament *A* became appreciable, because of conduction from the leads at bath temperature. Below, ~ 750° K., an increase in filament temperature due to radiation received from filament B (1200°) sets in

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[8] H. A. Jones and I. Langmuir, *G. E. Rev., 30,* 310, 354 (1927).

The lead cooling correction was calculated[9] and it was shown that though the temperature of the 3 cm long central part of the filament was reduced, the distribution remained uniform to $<1°$. The lead loss correction was $-3°$ at 550° K. and $-20°$ at 430° K., the lowest temperature used in measurements of atom evaporation.

The radiation correction was determined in two ways. First the change in resistance of the filament A was observed with B hot and cold, at various temperatures of A. Second, the current required to produce a given electron emission (μ_a constant) when filament B was hot and cold was observed. By comparison the true temperature of A with B hot was obtained. The radiation correction amounted to $+3°$ at 750° K. and $+50°$ at 430° K.

V. DETERMINATION OF σ_{A1}

Various low pressures ($\mu_a = 10^{11}$ to 10^{13}) of caesium were established and then filament A was maintained at a low temperature T_1 until trial showed that σ_A had reached its limiting steady value fixed by the balance between evaporation and condensation. In successive experiments, as T_1 was progressively lowered, it was found that σ_A, as given by the 2-filament method, increased at first rather rapidly and then very slowly until finally when T_1 was reduced below about 325° K. no further increase in σ_A occurred. This quite definite limiting value which was observed in numerous experiments was presumed to be the value σ_{A1} corresponding to a complete monatomic film. These experiments gave $\sigma_{A1} = (4.80 \pm 0.05) \times 10^{14}$ atoms cm^{-2}.

Intervals at higher temperatures (~400° K.) to allow possible favorable rearrangements by migration did not change σ_{A1}. Only by cooling the filament (by immersion of leads in liquid air) below the temperature (bath temperature) corresponding to saturated caesium vapor were other values of σ observed. These were greater than 4.8×10^{-14} and increased very rapidly as the filament was cooled below bath temperature. If the filament was now heated only slightly above bath temperature, $\sigma_{A1} = 4.8 \times 10^{-14}$ was again obtained.

In these experiments no detailed study was made of the conditions which give values of σ_A slightly lower than σ_{A1}. In later experiments, Section XII, the actual slow variation of σ with T and μ_a in this region was recorded and further justification is given for regarding this limiting value as that corresponding to a complete monatomic film.

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[9] I. Langmuir, S. MacLane and K. B. Blodgett, *Phys. Rev., 35,* 478 (1930).

VI. ANALYSIS OF EXPERIMENTAL DATA ON ATOM EVAPORATION

Fig. 8 gives the experimental data on atom evaporation. The apparent (observed) concentration of adsorbed caesium, σ_A, is plotted as a function of $1/T$. For each curve μ_a is constant and has the value indicated. The values of σ_A above 0.25×10^{14} were determined by the 2-filament method. Below 0.30×10^{14}, σ_A was determined by the direct flashing method. An enlarged plot of the lower σ_A data is also given.

The equation chosen for analysis of the data is

$$\ln \nu_a = A_a - B_a/T, \tag{6}$$

where A_a and B_a were functions of θ only. It has been shown theoretically[2] that A_a consists of two parts such that

$$A_a = A + S, \tag{7}$$

where

$$S = \ln \theta + 1/(1 - \theta) - \ln (1 - \theta). \tag{8}$$

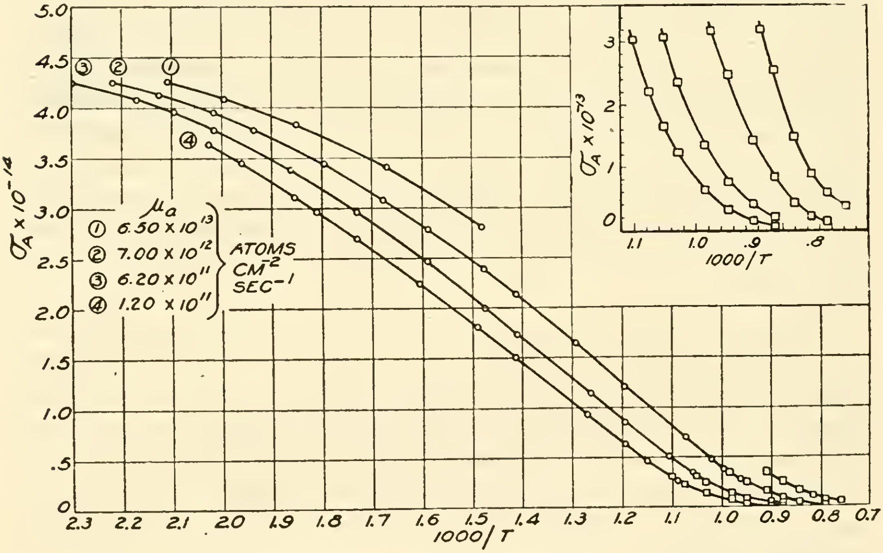

FIG. 8. Experimental data on atom evaporation. Observed concentration of caesium (σ_A) as a function of $1/T$.

The dependence of A and B_a on θ remained to be determined by the experiments.

If this form of equation is applicable to the observed data, then ($\ln \nu_a - S$) plotted as a function of 1/T, at any value of θ, should give straight lines of slope B_a and intercept A. With the values of ν_a ($= \mu_a$) and $1/T$ at various constant values of σ, read from the smooth curves (Fig. 8) drawn through the experimental points, such straight lines were obtained. The intercepts, A, showed a small variation with θ expressed empirically by

$$A = 61 + 4.8(\theta - \tfrac{1}{2}\theta^2). \tag{9}$$

With values of A and S from Eqs. (9) and (8) A_a was calculated as a function of θ. From these values of A_a and the observed values of ν_a and T from the data shown in Fig. 8, B_a was calculated by Eq. (6). For values of θ up to about 0.6, it was found empirically that B_a for all values of μ_a could be represented by

$$B_a = 32{,}380/(1 + 0.714\theta) \tag{10}$$

within the experimental error of about 0.3 percent. For larger θ's, B_a deviated from this expression slightly; however, the deviation was about 2 per cent at $\theta = 0.8$ and 4 per cent at $\theta = 0.9$.

The extent of the agreement of the values of B_a obtained from the experimental data with the empirical equation, Eq. (10), is shown in

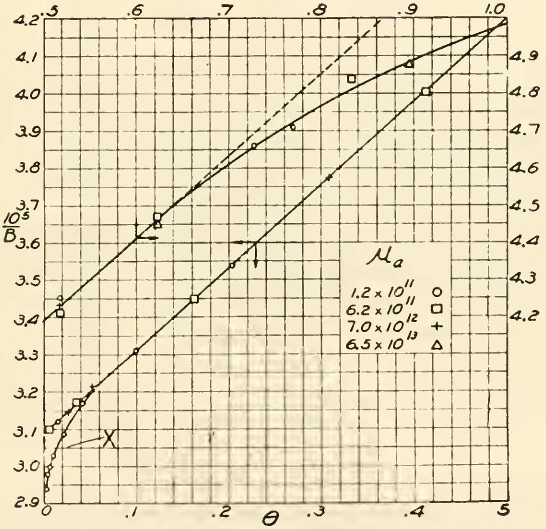

FIG. 9. Experimental variation of $1/B_a$ with θ. B_a is proportional to the heat of evaporation for atoms. X is the deviation caused by the active areas.

Fig. 9 which is a plot of $1/B_a$ against θ. If the data are to agree with Eq. (10), the points should lie on a straight line.

In the first analysis of the data by this method, values of $1/B_a$ were obtained which fitted Eq. (10) down to $\theta = 0.05$. Below this $1/B_a$ deviated as shown at X in Fig. 9. Such a deviation means that the observed values of ν_a were less than those calculated by Eq. (6) when using values of B_a from Eq. (10). At such low surface concentrations, repulsive forces between adatoms should begin to be inappreciable so that the equation of state of the adsorbed film on a *homogeneous* tungsten surface should approach that of an ideal 2-dimensional gas, *viz.*, $F = \sigma kT$. This would mean that the heat of evaporation measured by B_a should change very little with θ for these small values of θ. It seems possible to account for the increasingly rapid change in B_a at low θ as shown by curve X, only if the tungsten surface is not completely homogeneous. By trial it was found that this difficulty disappeared if it was assumed that 0.5 percent of the tungsten surface holds caesium so much more firmly than the rest that this *active surface* becomes saturated before more than 0.5 percent of the remaining surface is occupied. Thus the total concentration could be expressed as

$$\sigma_{\text{obs}} = \sigma_a + \sigma_n = \sigma_{A1}(\theta_a + \theta_n), \tag{11}$$

where the subscripts refer to the active and normal parts of the surface. When the active surface becomes saturated, so that $\theta_a = 0.005$,

$$\theta_n = \theta_{\text{obs}} - 0.005. \tag{12}$$

Calculating ν_a or $1/B_a$ from Eqs. (6) and (10) with θ_n instead of θ_{obs} gave agreement with experiment down to values of θ_n as low as 0.01, as shown by the points that lie along the straight line in Fig. 9. Any deviations which existed below this concentration were to be attributed to lack of saturation of the active surface, i.e., when $\theta_a < 0.005$.

The validity of Eqs. (6), (9) and (10) and likewise the precision of the experimental determinations of θ, is shown by the fact that the experimental points in Fig. 8 have an average deviation from the calculated curve of about 1° in T with no deviation greater than 3° up to $\theta \simeq 0.6$; at higher θ's the deviations vary from 2 to 15°.

For convenience in calculation, Eq. (6) may be written with common logs as

$$\log_{10} \nu_a = \mathbf{A}_a - \mathbf{B}_a/T \tag{13}$$

where $\mathbf{A}_a$ and $\mathbf{B}_a$ in heavy faced type represent the values of A_a and B_a (from Eqs. (7) and (10)) divided by 2.303. Table I in the first two columns contains values of $\mathbf{A}_a$ and $\mathbf{B}_a$. Up to $\theta = 0.6$ the tabulated values of $\mathbf{B}_a$ were calculated from Eq. (10). At higher θ's the experimental variation of $\mathbf{B}_a$ with θ was used as determined from Fig. 9. Complete explanation of the use of Table I will be given in Section X after electron and ion emission have also been discussed.

Fig. 10 shows θ_n as a function of $1/T$ (calculated through Table I) for a large range of values of μ_a.

Theory of adsorption by isolated active spots

If the isolated active areas are all alike and each is capable of holding only one adatom, the average life τ_a of an adatom on the active area is independent of σ_a. Since the probability per second for the evaporation of any adatom is $1/\tau_a$, the total rate of evaporation from the active areas is σ_a/τ_a.

TABLE I

DATA FOR CALCULATION OF EVAPORATION RATES

$$\text{Log}_{10}\, \nu = A - B/T$$

(Note that here common logs are used. To obtain values of A_a and B_a for use in Eqs. (6) to (10) multiply the tabulated values by 2.303.)

	Atoms (ν_a)		Ions (ν_p)		Electrons (ν_e) $A_e = 27.55$	
θ_n	A_a	B_a	A_p	B_p	B_e	V_c
0		14061.2		10293.6	23990	0.000
0.002	24.2328	14043.2	23.9318	10409	23853	.0268
.005	24.6401	14013.3	24.3391	10515.6	23716	.0540
.01	24.9558	13963.8	24.6549	10730.1	23452	.1064
.02	25.2859	13866	24.9849	11141.8	22941	.2079
.03	25.4913	13769	25.1904	11530	22457	.3038
.04	25.6459	13673	25.3450	11898	21992	.3960
.05	25.7719	13579	25.4709	12248	21549	.4840
.06	25.8804	13486	25.5795	12582	21122	.5686
.07	25.9764	13394	25.6755	12894	20719	.6487
.08	26.0633	13304	25.7623	13196	20325	.7267
.10	26.2179	13127	25.9169	13761	19584	.8738
.12	26.3556	12954	26.0546	14284	18888	1.012
.15	26.5388	12703	26.2379	15029	17893	1.2094
.20	26.8081	12306	26.507	16095	16429	1.500
.25	27.050	11934	26.749	17061	15089	1.7658
.30	27.276	11583	26.975	17907	13891	2.0034
.40	27.707	10939	27.406	19365	11792	2.420
.50	28.142	10364	27.841	20350	10230	2.73
.55	28.375	10098	28.069	20588	9726	2.83
.60	28.629	9849	28.328	20638	9424	2.89
.65	28.916	9623	28.612	20563	9272	2.92
.70	29.256	9425	28.955	20368	9272	2.92
.75	29.683	9256	29.377	20103	9373	2.90
.80	30.266	9110	29.965	19800	9524	2.87
.85	31.159	8985				
.90	32.821	8881				
.95	37.495	8798				
1.00		8733				

In a steady state this must be balanced by the rate of arrival of adatoms from the vapor phase. Since α for the surface as a whole is unity, we must assume that an incident atom whose path is directed towards an elementary space of the active area which is already occupied by an adatom, condenses in an adjacent vacant normal space. The total rate of arrival into the active

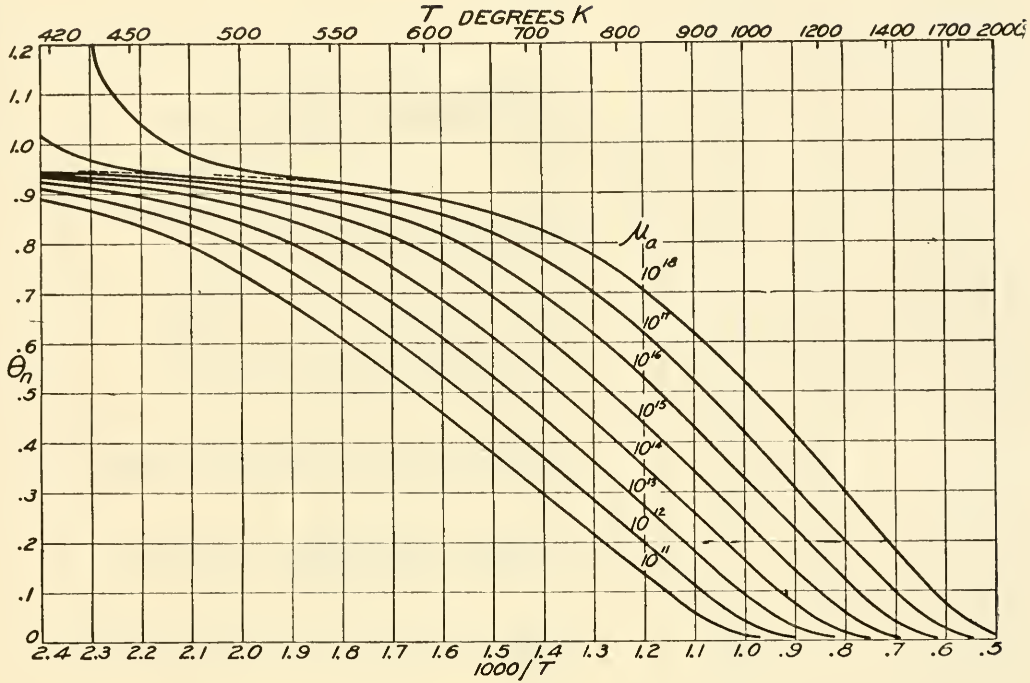

FIG. 10. Fraction (θ_n) of the tungsten surface covered with caesium at the temperature T; calculated (Eq. (6) or Table I) for different μ_a's. μ_a is proportional to caesium pressure.

areas from the vapor phase is thus $\mu(\theta_{a1} - \theta_a)$, where θ_{a1} is the maximum value of θ_a. Equating the rates of evaporation and condensation we have

$$\mu(\theta_{a1} - \theta_a)/\theta_a = \sigma_{a1}/\tau_a. \tag{14}$$

Langmuir has derived a general equation for the life of adatoms which may readily be put in the form [10]

$$\tau/\sigma_{a1} = 1.73 \times 10^{-27} M^{\frac{1}{2}} T_M{}^{-1} \epsilon^{b/T} \tag{15}$$

where T_M is the mean temperature over the range of validity of the equation. Taking $T_M = 800°$ and $M = 133$ (the atomic weight of Cs) and eliminating σ_{a1}/τ_a between this equation and Eq. (14) we obtain

$$\ln[\mu(\theta_{a1} - \theta_a)/\theta_a] = 65.8 - b/T.$$

With common logarithms this becomes

$$\log_{10}[\mu(\theta_{a1} - \theta_a)/\theta_a] = 28.58 - \mathbf{B}'/T. \tag{16}$$

In these equations θ_{a1} and $\mathbf{B}'$ should be constants the value we now wish to determine from our experimental data on θ_{obs} as a function of μ and T for very dilute caesium films. These data are given in the first three columns of Table II.

TABLE II

RELATION OF ADSORPTION ON ACTIVE AND ON NORMAL AREAS FOR DILUTE CAESIUM FILMS

1 μ_a	2 θ_{obs}	3 $10^3/T$	4 $\mathbf{A}_a$	5 $\mathbf{B}_a$	6 θ_n	7 θ_a	8 θ'	9 $\mathbf{B}'$
1.2×10^{11}	.00209	.891	23607	14059	.00048	.00161	.322	19306
	.00419	.925	24076	14050	.00141	.00278	.555	19020
	00628	.945	24345	14037	.00257	.00371	.742	19000
7.0×10^{12}	.00209	.775	23739	14058	.00065	.00144	.288	19797
	.00419	.810	24219	14043	.00195	.00224	.448	19328
	.00628	.828	24461	14030	.00337	.00291	.582	19188
	.01047	.850	24744	14000	.00630	.00417	.835	19388

A series of trials has shown that the best agreement of these data with Eq. (16) is obtained if we take $\theta_{a1} = 0.005$ as found in the preliminary analysis which led to Eq. (12).

Since μ can be expressed as a function of θ_n and T by Eqs. (6) to (10) or by Table I, we can by a series of approximations (or graphically) determine θ_n for each set of experimental values of μ and T. The values calculated in this way are given in the 6th column of Table II. Columns 4 and 5 contain values of $\mathbf{A}_a$ and $\mathbf{B}_a$ used in these calculations.

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[10] See reference 2. The above Eq. (15) is obtained by combining Eqs. (5), (6), (7) and (37) on pages 2799 and 2806.

Subtracting θ_n from θ_{obs} in accordance with Eq. (12) we obtain the values of θ_a given in the 7th column. The 8th column contains θ', the fraction of the active surface occupied by adatoms:

$$\theta' = \theta_a/\theta_{a1} = 200\theta_a.$$

The 9th column contains values of B′ calculated from Eq. (16) from the values of μ, θ_a, and T in the table. These results fully justify our assumption that B′ is independent of θ_a and indicate that the adatoms in the active areas are so far apart that they do not influence one another and therefore are to be regarded as isolated active spots. Eq. (16) becomes

$$\log_{10}[\mu(1-\theta')/\theta'] = 28.58 - 19{,}300/T. \qquad (17)$$

These "active" spots may be located at any reentrant angle between crystal planes or at irregularities in the lattice which may cause a Cs atom to be held more tightly than at other points. Thus the active area θ_{a1} will probably vary in extent depending on the grain size of the filament and on the heat treatment given. However, the properties of the normal surface will be unaffected. It is to be noted that Eq. (17) is in such a form as to be valid even if θ_{a1} should change.

VII. EQUATION OF STATE AND EVAPORATION EQUATION FOR THE ADSORBED Cs FILM

The equation of state of the two dimensional gas making up the adsorbed film was found theoretically[2] for molecules which repel as dipoles, by means of the Clausius virial. The forces are repulsive forces varying as the inverse 4th power of the distance (r) between adatoms. This equation gave the spreading force F in terms of θ, T, and the dipole moment M. By use of Gibbs' equation for the adsorption isotherm, the rate of evaporation of atoms ν_a could be expressed in terms of θ, T, and the spreading force F. These equations were of the form required by the experimental data. Therefore F and hence M could be calculated as functions of θ entirely from data on the evaporation of atoms.

The contact potential of the surface against that for pure tungsten could also be calculated from the relation.

$$V_c = 2\pi M\sigma(\text{c.g.s.}) = 1885 M\sigma_1\theta \text{ volts}. \qquad (18)$$

After obtaining V_c, the electron emission ν_e was calculated for any value of θ from the Boltzmann equation,

$$\nu_e/\nu_w = \exp(V_c e/kT) \qquad (19)$$

and Dushman's equation for ν_w, the electron emission from clean tungsten.

Likewise the rate of ion evaporation, ν_p, was calculable[11] with the aid of the Saha equation and was given by

$$\ln(2\nu_p) = \ln \nu_a + (e/kT)(V_w - V_i - V_c) \tag{20}$$

where V_w is the electron affinity of pure tungsten 4.62 volts, V_i is the ionizing potential of the caesium atoms 3.874 volts, and V_c is the contact potential as defined above. Thus from data on neutral atom evaporation (ν_a, θ, T) it was possible to calculate M, V_c, ν_e, and ν_p for comparison with the experimental values of these quantities. Further details and a tabulation of the calculated values of F, M, V_c, and other quantities included in the theoretical equations are given in reference 2.

VIII. CONTACT POTENTIAL AND ELECTRON EMISSION (EXPERIMENTAL)

The electron emission, ν_e, was measured from filament A at various filament temperatures and pressures of Cs. The relation between θ and pressure being known, the θ corresponding to each emission was also known. As a check in part of the runs, θ was determined immediately following the measurement of ν_e, by flashing to filament B (2-filament method).

The values of ν_e involved in the calculation of contact potentials from the Boltzmann Eq. (19) and for use in equations relating ν_e to ν_a and ν_p, must correspond to thermodynamic equilibrium and hence were measured at zero field. The effect of the external field on the electron emission from Cs coated tungsten is in general larger than for pure tungsten and varies with θ. Current-voltage data were taken for a series of constant temperatures and constant values of Cs pressure, corresponding to values of θ from 0.16 to 0.80. As shown in Fig. 11 there were sharp breaks in the plotted data and the value of ν_e at the break was taken to represent ν_e at zero field. The great variation of the effect with θ is readily seen. Fig. 12 shows that at high and low values of θ the variation of ν_e with voltage approaches that for clean tungsten. The largest departure is near $\theta = 0.55$ and decreases rapidly beyond a θ of about 0.65. The slopes below θ's of 0.30 were not measured accurately enough to show how rapidly the behavior of clean tungsten was approached at low θ. It should also be noted (Fig. 13) that the zero-field emission as obtained in this way may be far lower than that value obtained by extrapolating the normal higher voltage range Schottky slope to zero field as Dushman has done.[12]

To compare these electron emission data with the values calculated from

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[11] See reference 2.

[12] S. Dushman, *G. E. Rev.*, *26*, 157 (1923).

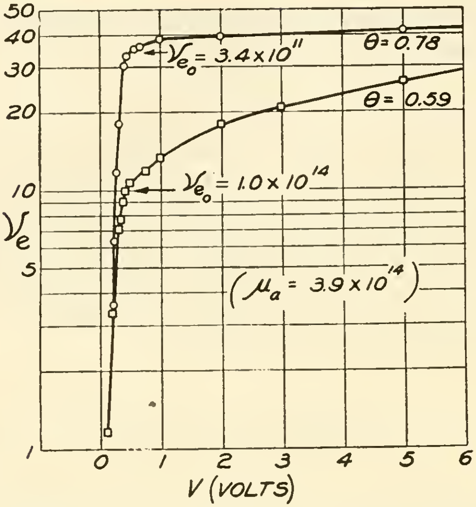

FIG. 11. Electron emission (ν_e) *vs.* voltage for Cs on W. Example of curves used to determine ν_e at zero field.

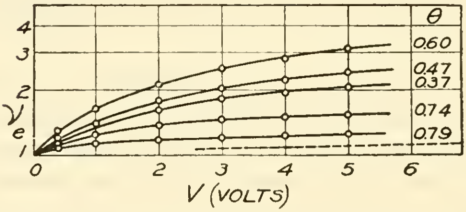

FIG. 12. Change of effect of external field on ν_e with θ. Dotted line indicates slope of curve for pure tungsten, $\theta = 0$.

experiments on atom evaporation as described in Section VII, the corresponding values of the contact potentials against a pure tungsten surface are plotted in Fig. 14 as functions of θ. The heavy line curve is calculated from data on ν_a by the methods described in Section VII, by using a temperature of 800° K. The values obtained with $T = 600°$ or $T = 1000°$ are practically identical with those at 800° (within about 0.02 volt for V_c). The points indicated by circles, etc., are the contact potentials calculated by Eq. (19), from the ratio of the observed electron emission to that from pure tungsten. The agreement is excellent up to θ of about 0.50. At this point the values obtained from ν_a deviate and show no maximum as do the points calculated from the observed electron emission. The deviation in this region is probably to be explained by a change in the law of force between adatoms as the atoms become crowded. The force varying as r^{-4}, as used in the theory, is evidently no longer adequate.

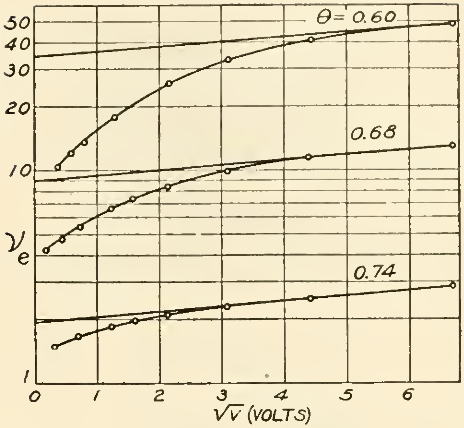

FIG. 13. Theoretical Schottky slope (straight lines) compared to actual course of current-voltage curves as zero field is approached.

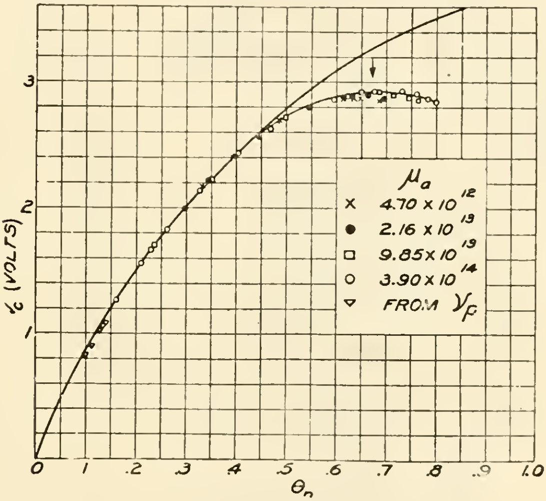

FIG. 14. Contact potential V_c. Variation with θ as determined from measurements of ν_e given by circles, etc. V_c from measurements of ν_p given by triangles. Values calculated from atom evaporation data given by heavier solid curve.

Table III contains the data on ν_e for a series of values of θ and T at four different Cs pressures, together with the contact potentials calculated from Eq. (19). Over the entire range of θ, T changed about 500°. At constant θ, ν_a varied about 100-fold and T changed 20 to 30° in going from the lowest to the highest Cs pressure. This small range of T prevents any conclusions as to the effect of temperature on the contact potentials. How-

TABLE III

DATA ON ELECTRON EMISSION AND CALCULATED CONTACT POTENTIAL

$\mu_a = 4.70\times10^{12}$				2.16×10^{13}				9.85×10^{13}				3.90×10^{14}			
T	θ	ν_e	V_c	T	θ	ν_e	V_c	T	θ	ν_e	V_c	T	θ	ν_e	V_c
774	.333	5×10^{10}	2.17	836	.298	7×10^{10}	1.99	928	.238	9×10^{10}	1.70	1050	.167	1.0×10^{11}	1.31
736	.392	3×10^{11}	2.41	801	.345	3.6×10^{11}	2.22	906	.264	2.4×10^{11}	1.85	1001	.211	2.5×10^{11}	1.56
677	.492	1.7×10^{12}	2.70	736	.443	3.7×10^{12}	2.57	836	.349	2.4×10^{12}	2.24	980	.231	4.5×10^{11}	1.66
613	.613	1.0×10^{12}	2.86	677	.545	9×10^{12}	2.80	736	.499	3.3×10^{13}	2.71	950	.263	1.0×10^{12}	1.82
604	.632	6×10^{11}	2.87	630	.631	3.8×10^{12}	2.89	677	.598	3.2×10^{13}	2.87	895	.327	6.2×10^{12}	2.14
596	.648	3.2×10^{11}	2.86	613	.663	1.5×10^{12}	2.89	661	.625	2.1×10^{13}	2.89	836	.402	3.1×10^{13}	2.43
586	.668	1.6×10^{11}	2.85	596	.696	4×10^{11}	2.87	646	.652	1.3×10^{13}	2.91	789	.467	7.6×10^{13}	2.62
578	.685	6.5×10^{10}	2.84					630	.682	5.6×10^{12}	2.91	707	.595	1.0×10^{14}	2.86
								613	.713	1.9×10^{12}	2.90	661	.673	4.2×10^{13}	2.93
								596	.745	3.7×10^{11}	2.87	630	.729	8.8×10^{12}	2.93
								586	.763	1.4×10^{11}	2.84	613	.755	2.3×10^{12}	2.93
												596	.783	3.4×10^{11}	2.86
												586	.797	1.6×10^{11}	2.85

ever, the value 2.8 volts, obtained by Langmuir and Kingdon,[13] for a heavily Cs coated filament, by direct measurement at ∼ 300° K., suggests there is no large dependence on temperature.

It is to be noted that the maximum V_e or ν_e occurs at $\theta = 0.67$ and decreases as θ approaches 1.0. As θ's of 0.5 to 0.6 are approached, the adsorbed Cs atoms begin to form a fairly continuous layer. The outer surface of the layer begins to have the properties of Cs and not those of a com-

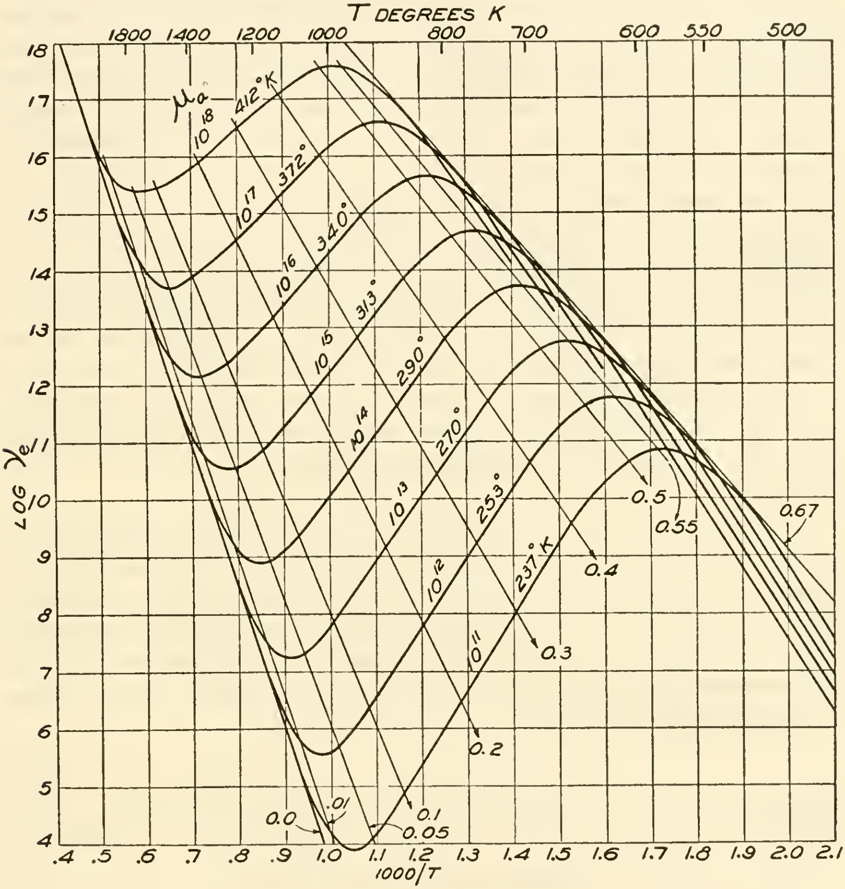

FIG. 15. Field-free electron emission (calculated) from a tungsten filament in equilibrium with Cs vapor at the filament temperature T. Rate of arrival (μ_a) of Cs and bath temperatures given on each curve. Pressure at 237° K is 6.7×10^{-7} baryes; at 412°K it is 8.8 baryes. Diagonal straight lines intersecting the curves give corresponding values of θ_n.

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[13] I. Langmuir and K. H. Kingdon, *Phys. Rev.*, *34*, 129 (1929).

posite surface of Cs and bare tungsten as is the case at lower θ's. At still higher values of θ the already crowded layer tends to be compressed and the adsorbed atoms are given in effect smaller atomic volumes. In general, smaller atomic volume is accompanied by lower electron emission. This may explain the decrease in ν_e at values of $\theta > 0.7$.

Since the values of contact potential from ν_a and ν_e agree so well below $\theta = 0.50$, the values from ν_a have been used with Eq. (19) to construct plots of ν_e *vs.* $1/T$ down to low values of θ. Fig. 15 shows a family of curves calculated for a series of values of μ_a. The curves were found for $\theta > 0.5$ by using the values of V_c taken from the smooth curve (Fig. 14) through the points calculated from ν_e. The highest (412° K.) corresponds to a pressure of 8.8 baryes; the lowest (237° K.) to 6.7×10^{-7} baryes. The curves at higher pressures may be compared with older unpublished data of Kingdon taken in the region of very low θ ($0 - 3$ percent), where the caesium emission approaches that of pure tungsten (ν_w). This is of particular interest because it may show whether the equations and constants obtained at the pressures of the present experiments can be used to calculate electron emissions at pressures many thousand times greater.

The comparison showed a difference of about 20 percent in the ratio ν_e/ν_w, the calculated values of ν_e/ν_w being lower. This is a satisfactory agreement considering the difficulty of making experiments at high pressures.

In connection with this comparison with the data of Kingdon, it is desired to correct certain equations and statements in the first paper by Langmuir and Kingdon [1] on the *Thermionic Effects Caused by Vapors of Alkali Metals.* In this work no scale of θ was available and an equation (Eq. (10), page (71)) from which θ had been eliminated was derived. This equation was to be applied in the region of very low θ. This equation in corrected form should be,

$$(\nu_e/\nu_w)^{a_1/c} \quad \ln (\nu_e/\nu_w) = (c/d)\nu_a \tag{21}$$

derived from the two approximate equations, valid for low values of θ,

$$\ln (\nu_a/\theta) = a + a_1\theta; \quad \ln (\nu_e/\theta) = c\theta.$$

The equations representing ν_a and ν_e in the present experiments have been put in this form and the constants determined.

$$a_1 = 23{,}100/T + 6.8; \quad \ln d = 62 - 32{,}380/T$$

$$a = 62 - 32380/T; \quad a_1/c = 0.188 + 5.53 \times 10^{-5}T.$$

$$c = 123{,}000/T.$$

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[1] I. Langmuir and K. H. Kingdon. Proc. of the Royal Soc., A, *107*, 61 (1925).

Calculations of ν_e or ν_e/ν_w from Eq. (21) give good agreement with the exact Eq. (19) up to θ of about 0.04. This treatment is probably applicable to dilute films in general.

In developing an equation of state, Gibbs' equation was given in a wrong form. Correctly it should be $dF/d \ln \nu_a = nkT$ as given in the present paper.

Fig. 1 in the paper by Langmuir and Kingdon shows electron emission curves plotted as in Fig. 15 of the present paper. The data of Langmuir and Kingdon were not corrected for the cooling effects of the filament leads and were not determined for zero field. Comparison of corresponding points shows emissions in Fig. 15 to be 1/3 to 1/8 of those found by Langmuir and Kingdon.

IX. POSITIVE ION EVAPORATION (EXPERIMENTAL)

The rate of ion evaporation was also studied as a function of filament temperature and θ at various pressures of caesium. The emission varies with field about as much as for electron emission; ν_p at zero field was obtained in the same manner as for ν_e, although (Fig. 16), the break in the

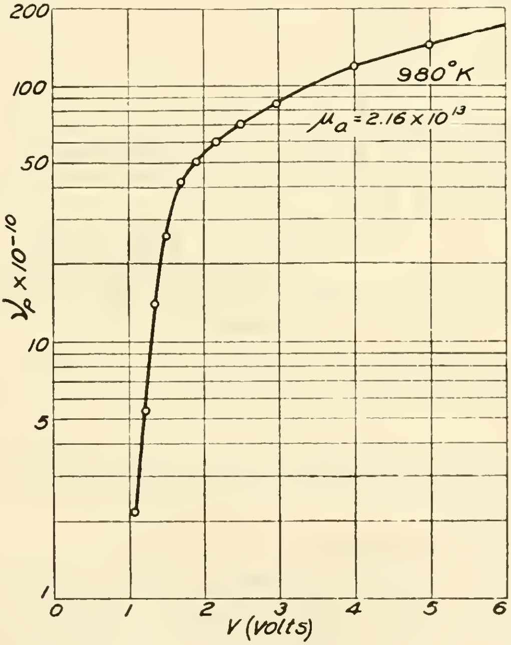

Fig. 16. Current voltage data for positive ion evaporation.

log ν_p *vs.* voltage curve was not as readily determined. For this reason a slightly different method was also employed. The voltage required to keep ν_p constant as the filament temperature was varied was found to change rapidly as the zero of potential was approached, thus allowing a closer estimate of ν_p at zero field, by choosing the point of greatest curvature. Fig. 17. Since $\mu_a = \nu_a + \nu_p$, θ could be found for any value of ν_p from the known relation between ν_a and θ. To compare with the theoretical value of ν_p, Eq. (20) was used together with ln $\nu_{p\ \mathrm{obs}}$ to calculate the contact potential V_c. The points in Fig. 14 in the region $\theta = 0.10$ to 0.14 were so calculated. The disagreement is not greater than might correspond to errors in obtaining ν_p at zero field.

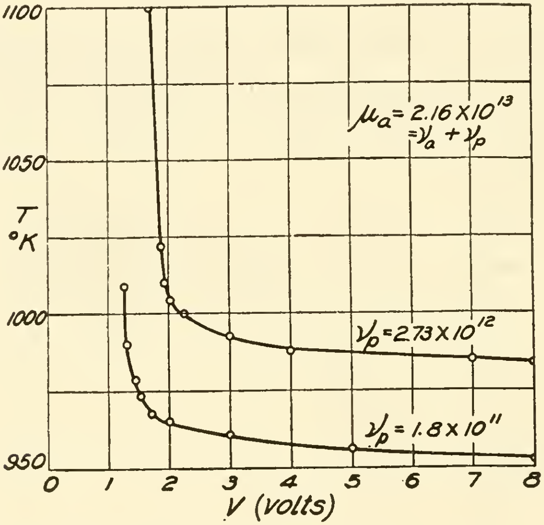

FIG. 17. Temperature voltage data for constant ν_p. Curves used to determine ν_p at zero field.

In connection with the study of positive ion evaporation rates as a function of θ, the following general characteristics of positive ion evaporation may be given.

Fig. 18 shows the exponential increase of ν_p with temperature at constant values of $\mu_a (= \nu_a + \nu_p)$. Depending on the pressure, a discontinuity sets in at a fairly definite critical temperature (which increases with μ_a) and ν_p rises at a constant rate until the value characteristic of a clean tungsten filament is reached. The variation of this maximum value of ν_p with temperature and the external field is discussed in Section XI. The discontinuity has been observed previously by Langmuir and Kingdon,[1] Killian[14] and Becker.[3] Langmuir and Kingdon[1] have shown that this discontinuity indicates the existence of caesium in two surface phases.

Becker[3] was the first to point out that the existence of the two stable phases was a consequence of the relation between $\nu_a + \nu_p$ and θ.

Fig. 19 shows both atom and ion evaporation rates (calculated) in the region where ν_a and ν_p are of comparable magnitude. The full line *ABC* gives the sum of atom and ion rates from a tungsten filament at 848° K. in caesium vapor and exposed to an accelerating field for ions. It is seen that for constant values of $\mu_a (= \nu_a + \nu_p)$ there are three values of θ, as indicated, for example, by the intersections of the dotted line with the curve. Thus at a given pressure two values of θ may exist corresponding to two phases, a dilute (β) and a concentrated (α) phase. The intermediate θ is unstable. These phases are separated by a distinct boundary whose movement gives the observed rate of change of ν_p at the discontinuity. Migration has been shown to exist at the boundary between the phases and the velocity of propagation has been used to measure *D*, the coefficient of surface diffusion in a recent note[15] by the authors.

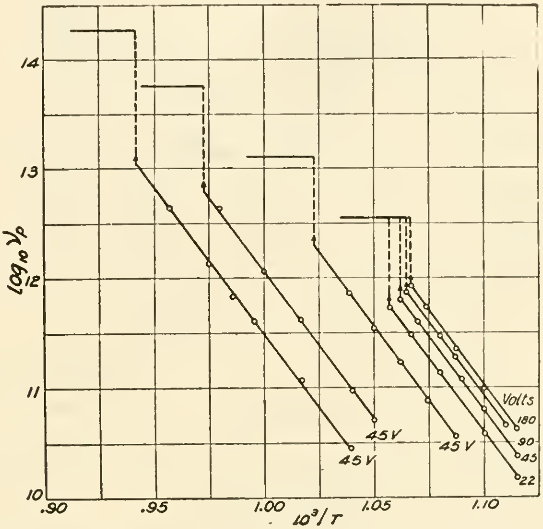

FIG. 18. Exponential increase of positive ion evaporation rate followed by discontinuous rise to maximum value of ν_p, ($\nu_p = \mu_a$).

The dotted line in Fig. 19 and *ABC* enclose the two areas X_1 and X_2.

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[14] T. J. Killian, *Phys. Rev.*, *27*, 578 (1926).

[15] I. Langmuir and J. B. Taylor, *Phys. Rev.*, *40*, 463 (1932).

Mathematical analysis [16] shows that the condition for a stationary boundary (when D, the surface diffusion coefficient, can be taken to be independent of θ) is that $X_1 = X_2$ when $(\nu_a + \nu_p)$ is plotted as a function of θ. The dotted line in Fig. 19 has been so drawn. If μ_a is raised, the concentrated α phase will appear. The velocity of motion depends on the displacement of μ_a.

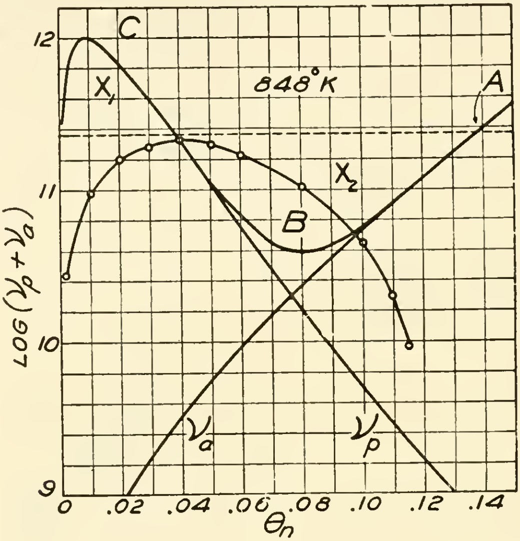

FIG. 19. Atom (ν_a) and ion (ν_p) evaporation rates for zero field at the lower values of θ. (Calculated at 848°K.) Circles give observed data under conditions as described in text.

Boundaries are established by the formation and growth of nuclei at slight inhomogeneities of the surface on which θ man increase or decrease more rapidly than on neighboring areas. Nucleus growth is not possible above point A in Fig. 19 since the dilute β phase is unstable. It may and does occur for any value of μ_a producing a θ between points A and B. The μ_a or θ at which formation and growth begin depends on the surface conditions and on how rapidly μ_a (or θ) is varied.

In particular, in Fig. 18 the points where a discontinuity sets in depend entirely on this accidental nucleus formation and have no other significance. A detailed comparison of these points in Fig. 18 with the curves of Fig. 19 is difficult since ν_p in the former is affected by the field, whereas the latter curves represent field free emission of ions.

As previously discussed (Section IV), a series of ion evaporation experiments were carried out with the bulb in liquid air so that μ_a was negligible. The rate was changed by aging from an irregular to a uniform variation with θ (Fig. 7). These experiments may now be explained more fully. Since μ_a is negligible, there is no mechanism for stopping the growth of newly formed nuclei after θ's lower than those corresponding to the level of point C are reached ($\sim$0.18 per cent for Fig. 19). The rate of evaporation will increase rapidly as the perimeter (boundary) of the nucleus increases, and fall off when two advancing boundaries meet. Each peak in Fig. 7 may be formed by this process. A new peak is formed as other nuclei increase their perimeters. Diffusion at the boundaries from the concentrated to the dilute phases speeds the process.

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[16] I. Langmuir, *Jour. Chem. Phys.*, *1*, 3 (1933).

These conclusions were verified by experiments in which, after one or more peaks in the evaporation rate had been passed, the field was reversed so that only atoms could evaporate (very slowly in the region $B-C$). After waiting several minutes the field was again reversed and ions allowed to evaporate. The ion evaporation, however, did not proceed at the previous rate but at a rate two or three times as great. This was because θ had been made uniform, by migration from areas of high θ to those already cleared by the first peaks. A uniform low θ could also be produced by coating the clean filament in a retarding field for ions. Here again, on reversing the field, the values of ν_p were larger than when the same total θ was reached by ion evaporation.

It is emphasized that the inhomogeneities needed to serve as nuclei for these discontinuous boundary effects do not compose any appreciable part of the tungsten surface. They are probably crystal boundaries or irregularities in these boundaries and need occupy no more than the one-half percent of surface discovered in the analysis of the atom evaporation data. That the effects are not accidental, such as might be caused by gas covered areas, is shown by the exact repetition of the peaks in numbers of experiments made at any stage in the aging process. Aging probably removed certain of the inhomogeneities and caused the rest to become sufficiently uniformly distributed to produce a regular evaporation rate.

As further evidence that the smooth curve finally obtained is still disturbed by the formation and growth of nuclei and does not represent the true variation of ν_p with θ, the observed values of ν_p have also been plotted (circles) in Fig. 19. At higher values of θ, $\nu_{p\text{ obs}} > \nu_{p\text{ calc}}$. This is due to the formation of nuclei and boundaries as just explained. At lower values of θ, $\nu_{p\text{ obs}} < \nu_{p\text{ calc}}$. This is because the high rate of evaporation from the few remaining concentrated patches is finally overbalanced by the practically zero rate from the large areas of nearly bare tungsten. Thus the observed maximum at $\theta \sim 0.04$ and the whole behavior of $\nu_{p(\text{obs})}$ depends on the average of the rates from these two (concentrated and dilute) phases and on the displacement of the phase boundary. The surface at

$\theta_{\text{obs}} = 0.04$ is made up of patches whose concentration is greater than that corresponding to $\theta = 0.04$ and areas of nearly bare tungsten.

Although the above types of experiments may give us a more detailed picture of the tungsten surface, it must be concluded that they are not suited for studies of ν_p from the main homogeneous part of the tungsten surface. As already shown, experiments made under steady conditions ($\nu_p + \nu_a = \mu_a$) do give values of ν_p in accord with theory.

The films obtained in the manner described above by evaporation of ions in accelerating fields illustrate the existence under these conditions of films which do not conform to the surface phase postulate.[17]

Killian [14] has obtained current-voltage characteristics for potassium and rubidium ions in the region of space charge limitation. He showed that the theoretical equation was followed and also gave curves exhibiting a remarkably sharp break at the saturation voltage. Figs. 20 and 21 were obtained for caesium ions and electrons in the present investigation. To avoid question as to the correct zero of potential the 2/3 power of the current has been plotted against the voltage. The break at saturation for ions is so sharp that it can be almost entirely accounted for by the small voltage drop along the central part of the filament. For electrons the transition occurs much more gradually and must have another explanation. With the masses of the electron and of the single Cs atom, the theoretical slopes were calculated. For electrons the calculated slope was 1.14×16^{-3} and the observed 1.05×10^{-3}. For ions the calculated slope was 1.82×10^{-5} and the observed value was 1.65×10^{-5}. The agreement is satisfactory since

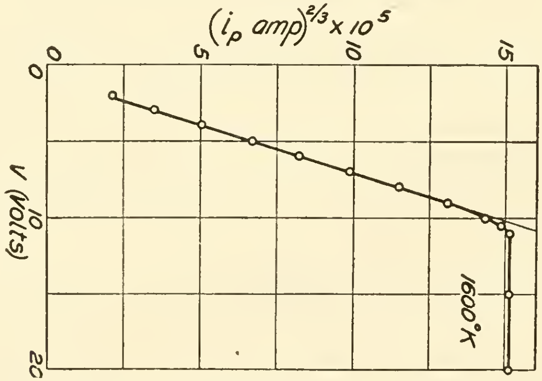

Fig. 20. Positive ion currents limited by space charge for Cs ions.

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[17] A more detailed analysis of this postulate and its implications in connection with a phase rule for adsorption has been presented by I. Langmuir, in reference 16.

no attempt was made to correct for the influence of the second filament held at the potential of the first in these experiments. The second filament, acting as a grid, would decrease the observed emissions and hence the slopes as found. The theoretical ratio of ion to electron slopes is 62.6 and the observed value was 63.6.

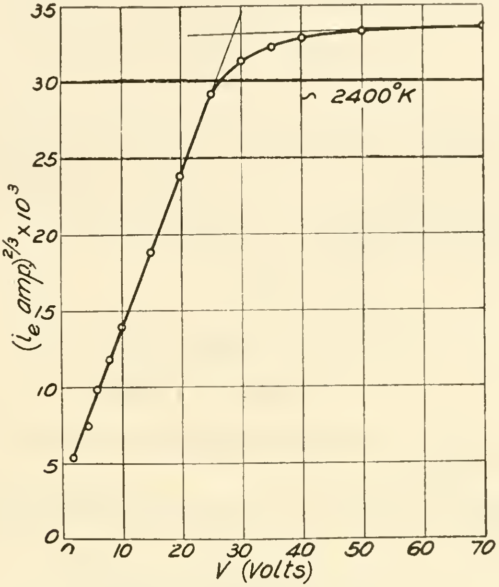

FIG. 21. Electron currents limited by space charge from clean tungsten.

An equation, similar to Eq. (21), for the rate of positive ion evaporation at very low θ's may be developed

$$\begin{aligned} \ln (\nu_p/\theta) &= b + b_1\theta, \\ b &= 61.31 - 23{,}699/T, \\ b_1 &= 6.80 - 99{,}900/T. \end{aligned} \tag{22}$$

This equation gives ν_p within one percent up to approximately $\theta = 0.02$. The limit of application is near $\theta = 0.03$ where the error is about 15 percent. By differentiation an expression giving the position of the maximum in the ν_p *vs.* θ curve is obtained

$$\theta_{\max} = T/(99{,}900 - 6.8T) \tag{23}$$

at 500° K., 1000° K., and 2000° K., $\theta_{\max}$ is 0.00513, 0.01075 and 0.0232.

X. GENERAL METHODS FOR CALCULATION OF ν, θ AND T

Table I has been given to simplify calculations of ν, θ and T. In the construction of this table the type of equation

$$\log_{10} \nu = \mathbf{A} - \mathbf{B}/T \tag{24}$$

was used, where for use in the equation with common logs

$$\mathbf{A} = A/2.303 \quad \text{and} \quad \mathbf{B} = B/2.303. \tag{25}$$

For example, A_a and B_a (for atom evaporation) refer to Eq. (1) as previously given with natural logs, $\ln \nu = A - (B\ T)$. A_a and B_a have been calculated from Eqs. (7), (8), (9) and (10), which give their dependence on θ. In addition, the corresponding quantities have been calculated for positive ion emission. For ion emission,

$$\begin{aligned} A_p &= A_a - \ln 2, \\ B_p &= B_a + 11{,}606(V_c + V_i - V_w) \\ &= B_a - 8681 + 11{,}606 V_c, \end{aligned}$$

as given by Eq. (20). For electron emission the Boltzmann equation gives $\ln \nu_e = \ln \nu_w + V_c e/kT$.

In the range 600°–1000° K. the electron emission from tungsten is very closely given by

$$\ln \nu_w = 63.44 - 4.76 e/kT.^* \tag{26}$$

Therefore

$$\ln \nu_e = 63.44 - (e/kT)(4.76 - V_c)$$

or

$$A_e = 63.44, \quad B_e = 11{,}606(4.76 - V_c).$$

The contact potential (V_c) was calculated from atom evaporation data for $\theta < 0.5$ and from emission data for $\theta > 0.5$.

Here also the above values of A and B are for the equations with natural logarithms of ν, ($\ln \nu$). The **A**'s and **B**'s in Table I have been converted (by Eq. (25)) for use in the equation with logarithm to the base ten.

As an example of the use of the table, in Fig. 22, ν_a, ν_p, and ν_e have been calculated and plotted as functions of θ at the constant temperature 1000° K. Fig. 19 is a similar example. Fig. 22 gives the relations between

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* See reference 2, Eqs. (7) and (98).

ν_e, ν_p, and ν_a as θ changes. The curves are calculated for 1000° K. but their general course is similar at other temperatures.

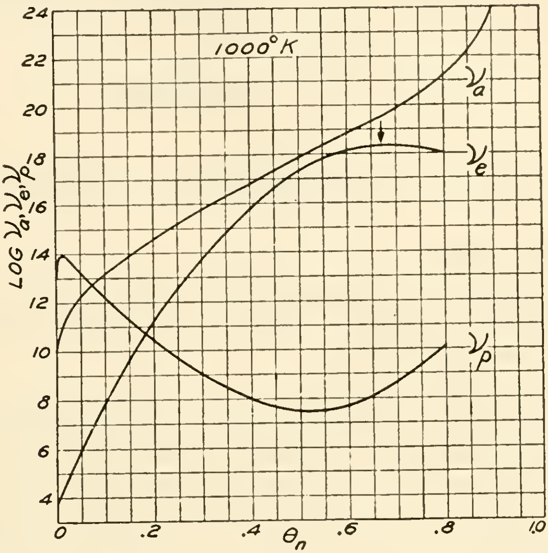

FIG. 22. Atom (ν_a), ion (ν_p), and electron (ν_e) evaporation rates at 1000°K, with zero field.

Heats of evaporation, according to the Clapeyron equation, are given by $b_0 = -k[d \ln p/d(1/T)]$ and are obtained for atoms, ions and electrons at any value of θ as follows:

$$b_0 = 1.987[2.303\mathbf{B} + T/2] \text{ calories}$$

$$= \frac{2.303\mathbf{B} + T/2}{11{,}606} \text{ volts,}$$

where **B** is $\mathbf{B}_a$ for atoms $\mathbf{B}_p$ for ions, and $\mathbf{B}_e$ for electrons. The term $T/2$ is introduced when Eq. (24) is changed to a form containing the pressure (p) instead of the rate (ν) in accord with Eq. (5), in order to calculate b_0 as given by the Clapeyron equation. T may be taken as $T_m = 800°$, the average filament temperature in the range (600–1200° K.) ordinarily used. $T/2$ corresponds at most to only a few hundredths of a volt.

The work function for electrons, i.e., the exponent (V_e) in an equation of the Dushman type

$$\nu_e = KT^2 \exp(-V_e e/kT)$$

is

$$V_e = (2.303\mathbf{B}_e - 2T_m)/11{,}606 \text{ volts.}$$

A similar equation containing B_p gives the work function (V_p) for ions. The term $2T_m$ corrects for the simplification made in adopting Eq. (26). Also $V_e = V_w - V_c$, where V_w is the work function (4.622 volts) for pure tungsten and V_c is the contact potential. It is to be noted that

$$V_e = (b_{oe} - (5/2)T)/11{,}606 \text{ volts.}$$

XI. THE CONDENSATION COEFFICIENT α AND TRANSIENT PHENOMENA

Concept of surface phase

Each phase in a heterogeneous equilibrium has properties which are uniquely determined by a definite number of parameters such as composition, temperature, pressure, etc.

If similar factors determine the properties of adsorbed films of caesium on tungsten, we may expect that all the properties of such a film would be uniquely determined by θ and T. On the other hand, one may well conceive of conditions under which the properties would depend on many other factors. For example, it is possible that the surface of the underlying tungsten may vary according to its method of preparation so that the rate of evaporation of caesium atoms from different tungsten surfaces would differ even if θ and T were the same. Or again, if a caesium film with given θ is formed in two different ways, as, for example, by condensation on to a bare surface or by evaporation from a more concentrated film, the distribution of Cs atoms over the surface might be different and thus cause variations in the properties. The properties could thus depend upon whether or not the film is in equilibrium with the surrounding Cs vapor.

It will be very useful, however, to look upon the unique dependence of the properties on θ and T as an ideal case which may be approached under favorable conditions. Let us, therefore, consider the properties of adsorbed films which conform to the following postulate.

Surface phase postulate: All the properties of an adsorbed film on an underlying surface of given composition are uniquely determined by θ and T

If this condition is fulfilled, ν_a, ν_p and ν_e are functions of θ and T only, *even if the film is not in equilibrium with the vapor phase.* The adsorbed film in equilibrium with caesium vapor is thus a system possessing two degrees of freedom in the sense of the phase rule.[16]

Under non-equilibrium conditions we then have

$$d\sigma/dt = \alpha_a\mu_a + \alpha_p\mu_p - \nu_a - \nu_p. \qquad (27)$$

Case I. Retarding field for ions. Under these conditions the ions which evaporate must all be brought back to the filament surface by the field so that if there is no external source of ions,

$$\alpha_p \mu_p = \nu_p \tag{28}$$

and therefore Eq. (27) becomes

$$d\sigma/dt = \alpha_a \mu_a - \nu_a. \tag{29}$$

Under steady conditions we then have

$$\alpha_a \mu_a = \nu_a. \tag{30}$$

Case II. Accelerating field for ions. In this case $\mu_p = 0$ so that

$$d\sigma/dt = \alpha_a \mu_a - \nu_a - \nu_p. \tag{31}$$

In a steady state we have

$$\nu_p = \alpha_a \mu_a - \nu_a. \tag{32}$$

Determination of $\alpha_a \mu_a$ from the ion current

According to Eq. (32), the value $\alpha_a \mu_a$ can be calculated from the positive ion saturation current density I_p by the relation

$$\alpha_a \mu_a = (I_p/e)(1 + \nu_a/\nu_p). \tag{33}$$

At high filament temperatures θ becomes very small and ν_a/ν_p approaches a limiting value which may readily be obtained from Eq. (20) by putting $V_c = 0$. Inserting numerical values of V_w and V_i we thus find

$$\log_{10} (\nu_a/2\nu_p) = -3770/T. \tag{34}$$

The value of ν_p in this equation is that corresponding to zero field. In experimental determinations of I_p to measure $\alpha_a \mu_a$ we usually employed a potential of -45 volts on the cylinders. Such fields (about 3000 volts per cm at the cathode) have been shown (at constant θ) to increase ν_p about 7-fold without having any effect on ν_a. Thus the ratio ν_a/ν_p corresponding to experimental conditions should be 1/7 of that given by Eq. (34). We thus calculate that ν_a/ν_p in Eq. (33) should have values that range from 2.1×10^{-4} at $T = 1200°$ to 5.8×10^{-4} at $1400°$. The errors involved in neglecting ν_a/ν_p in Eq. (33) are therefore negligible.

The experimental data given in Table IV were obtained to test this conclusion. The 2nd column gives the galvanometer deflection (300 = 0.027 microampere) produced by the ion current obtained with 45 volts on the cylinder, with the filament temperatures given in the first column.

TABLE IV

Experimental Test of Constancy of the Ion Current at High Filament Temperatures

Voltage = 45; $E = 3000$ volts cm^{-1}; caesium pressure 2.4×10^{-5} baryes; $\alpha_a \mu_a = 3.4 \times 10^{12}$.

T °K	i_p galv. defl.	i_{photo}	$i_{\text{photo}} + 300.3$	θ_n
1143	300	0.02	300.3	1.2×10^{-6}
1307	300	0.50	300.8	8.6×10^{-8}
1380	302	1.5	301.8	3.3×10^{-8}
1457	305	4.6	304.9	1.3×10^{-8}
1591	325	23.1	323.4	3.4×10^{-9}
1717	381	87	387	1.1×10^{-9}
1839	560	255	555	4.6×10^{-10}

It is seen that from 1143° to nearly 1400° the current remains remarkably constant, but rises increasingly rapidly at higher temperatures. This rise has been found to be due to photoelectric emission from the adsorbed caesium film on the cylinder under the influence of the light radiated from the filament. Such photoelectric emission is also observed when light is allowed to fall on the tube.

Since the light intensity of each wave-length varies in accord with Wein's law, the logarithm of the intensity is a linear function of the reciprocal of the filament temperature, the slope of the line, for natural logarithms, being C_2/λ, where the radiation constant C_2 is 1.433 cm deg. Analyzing the data for i_p in Table IV it is found, in fact, that the observed current i_p can be resolved into two parts, one having the constant value 300.3, and the other, the photoelectric current, being given by

$$\log_{10} (i_{\text{photo}}) = 9.08 - 12{,}270/T. \tag{35}$$

The 3rd column contains values of i_{photo} calculated by this equation. The 4th column shows that the sum of these two currents, $300.3 + i_{\text{photo}}$ agrees well with the observed value of i_p.

By immersing the bulb in liquid air the ion current became zero, but the photocurrents remained and were found to be 15 per cent lower than those given by Eq. (35), so that the constant 9.08 in this equation needed merely to be changed to 9.01.

Repeating the experiments of Table IV, with -310 volts on the collector instead of -45, gave currents which, analyzed in the same way, gave a constant ion current having the same value (300.3) as before, but gave photocurrents 2.2 times as great as with the weaker field, the coefficient of $1/T$ in Eq. (35) being unchanged. By placing the bulb in liquid air these photocurrents were reduced as before by 15 percent.

The effect wave-length of the radiation producing these photocurrents (a kind of Crova wave-length) can be determined by equating the coefficient of $1/T$ in Eq. (35) to $2.303 \times C_2/\lambda$; it is found to be 5070A, which is reasonable for caesium photoelectric cells.

We may estimate the magnitude of θ under the conditions of the experiments of Table IV by the limiting form (as θ approaches zero) of Eq. (22),

$$\log_{10}(\nu_p/\theta_n) = 26.625 - 10{,}294/T. \tag{36}$$

Here ν_p is the ion evaporation rate without accelerating field. Since in these experiments ν_p, which was equal to μ_a, was increased 7-fold by the field, we may put $\nu_p = 4.9 \times 10^{11}$ in Eq. (36). The values of θ_n, calculated in this way, are given in the last column of Table IV. For such low values of θ, ν_e cannot differ appreciably from that for a pure tungsten surface, so that the assumptions made in deriving Eq. (34) are justified.

The experiments thus indicate that within the experimental error of about 0.2 per cent the saturation ion current is independent of temperature and of field strength for ranges of temperature from 1200 to 1500° and for fields from 3000 to 20,000 volts cm^{-1}.

We must conclude from both theory and experiment that the ion saturation current method provides an extremely accurate measurement of $\alpha_o\mu_a$; where α_o is the value of α_a for very small values of θ.

Methods for the experimental determination of α_a and α_p

If, now, we had some independent means of determining the vapor pressure of caesium, from which we can calculate μ_a, we could determine α_o from our knowledge of $\alpha_o\mu_a$. However, as none of the available vapor pressure methods appears to be comparable in accuracy or sensitivity with that of the measurement of ν_p, we need to investigate other ways of finding α_a.

Experimental data, such as that of Table IV, which were also obtained for a wide range of other values of μ_a, *prove that* α_o *is strictly independent of temperature* in the range from about 1000 to 1500°, and *is independent of E, the accelerating field.* This suggests strongly that α_o is unity since any smaller value would probably vary with temperature. There are, however, other methods open to us for measuring α_a.

(1) *Direct flashing method.* Caesium is allowed to accumulate on the filament at a temperature T_1 at which ν_a is negligibly small, at the rate $\alpha_a\mu_a$. After a time t, σ_A is measured by the D.F. method (see Section III and Fig. 4). $\sigma_A = \bar{\alpha}_{av}\mu_a t$ where α_{av} is an average value of α_a over the range in θ from 0 up to the final value at time t.

Fig. 23 gives some typical data with the filament during accumulation at 300°, at 970° and 1001°.

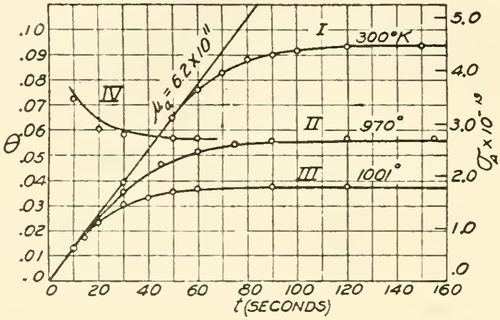

FIG. 23. σ_A *vs.* time at 300°, 970° and 1001°K, for $\mu_a = 6.20 \times 10^{11}$. Data obtained by direct flashing method for use in measuring α_a.

Each experimental point shown for curves I, II and III corresponds to a separate run in which the caesium was allowed to accumulate for the time t after cleaning the filament by flashing. The straight line drawn through the origin has been drawn with a slope equal to $\alpha_o\mu_a$ as determined by this steady ion current method. The experimentally determined points are seen to lie quite accurately on these lines at sufficiently low values of θ. We shall see that at 970 and 1001° the deviations from the straight line at the higher θ's in curves II and III agree with those calculated from the known evaporation rates of these films at those high temperatures.

The data obtained with the filament at 300° K. during the accumulation time, curve I, show that the observed points lie quite accurately on the straight line through the origin up to values of θ of about 0.07. The deviations at higher θ are due to evaporation of Cs as atoms during the flashing. This is shown by the fact that the curve remains entirely unchanged if T_1 is varied from 300 to 800° K., but the deviations do depend slightly on the flashing temperature and on the rapidity with which the temperature is raised. The direct flashing method is thus only applicable for values of θ up to about 0.08.

The fact that the experimental points lie on the straight lines of slope $\alpha_o\mu_a$ for sufficiently small θ proves that $\alpha_{av}\mu_a t$ equals $\alpha_o\mu_a t$. We conclude that for temperatures up to about 800° and for values of θ up to 0.07, α_a is constant and equal to α_0 within the experimental error of less than 1 percent. At 970° the same conclusion may be drawn up to $\theta = 0.02$.

(2) *Two filament method.* After allowing caesium to accumulate on filament A at temperature T_1 up to a definite value of $\sigma_A = \alpha_{av}\mu_a t$, σ_A is measured by the two filament method. If Q represents the quantity of

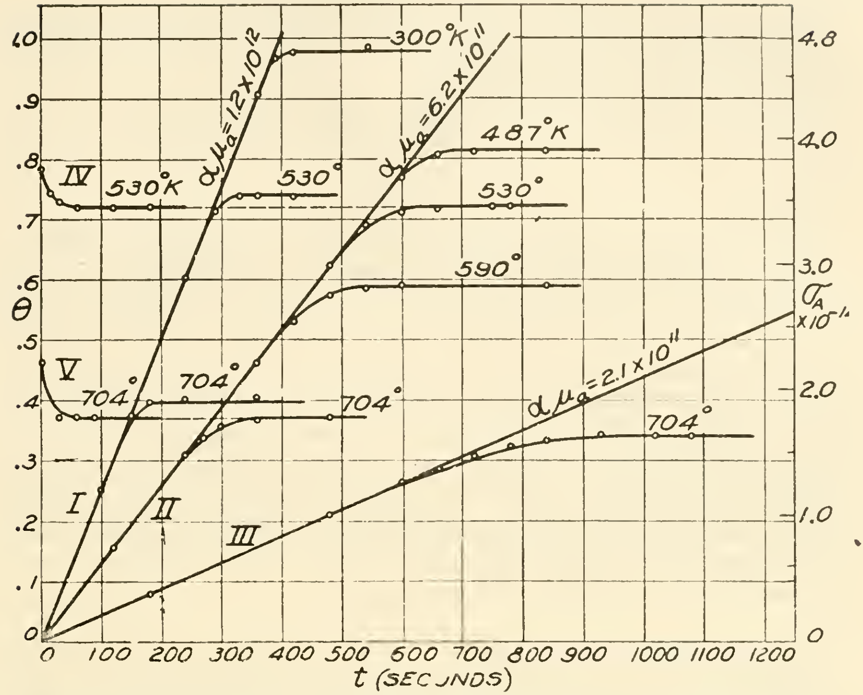

FIG. 24. σ_A *vs.* time at various filament temperatures and Cs pressures (μ_a) as indicated. Data obtained by two filament method for use in measuring α_a.

electricity corresponding to the observed ballistic kick produced when *A* is flashed, we have

$$Q = \alpha_{av}\mu_a t S_A f \alpha_o e, \qquad (37)$$

where S_A is the apparent surface area of the filament *A* within the cylinder C_o, and e is the electron charge. By dividing *Q* by $S_A fe$, we thus obtain values of $\alpha_{av}\alpha_o\mu_a t$.

The experimental points shown in Fig. 24 represent data obtained by this method for a series of relatively low filament temperatures, *viz.*, 300, 487, 530, 590 and 704° K. and with three different caesium pressures which gave, by the steady ion current method, values of $\alpha_o\mu_a$ of 1.20×10^{12}, 2.1×10^{11} and 6.2×10^{11} atoms $\text{cm}^{-2}\ \text{sec.}^{-1}$.

The straight lines marked I, II and III which pass through the origin have been drawn with slopes $\alpha_o\mu_a$ as determined by the steady ion current method. It is seen that the observed points, for sufficiently low θ, lie within the experimental error on the straight lines. Since the ordinates of the experimental points are $\alpha_{av}\alpha_o\mu_a t$, while those of the straight lines are $\alpha_o\mu_a t$, this agreement proves that $\alpha_{av} = 1$ and therefore $\alpha_a = 1$ for values of θ up to 0.98. We shall see that the deviations of the observed points from these straight lines as θ approaches a limiting value, are due to evaporation and do not indicate values of α_a less than unity.

In the next section we shall discuss the theoretical significance of the experimental fact that $\alpha_a = 1$ up to nearly $\theta = 1$.

Value of α_p

Moon[18] has shown that when a beam of Cs ions (without Cs atoms) is directed against a tungsten filament heated to high temperatures, no net current flows to the filament if there is a field near the filament which draws away ions. Without this field, or at a lower filament temperature, a current is observed which presumably measures the number of ions which strike the filament. Moon concludes that *all* of the ions which condense on the very hot filament leave it again as ions (none as atoms). This is a proof that ν_a/ν_p is very small, but does not necessarily prove that $\alpha_p = 1$, although it makes this probable. In view of the strong attractive forces between the ions and the tungsten surface (image force) it is, however, almost certain that there cannot be any appreciable reflection of low velocity ions, and we may safely conclude that $\alpha_p = 1$.

Transient effects in atom evaporation

We use the term *transient effects* to describe the phenomena involving changes in θ as distinguished from *steady* states in which θ stays constant. The accumulation periods which we have discussed correspond to transient states in which ν_a and ν_p are negligible compared to μ_a. Let us now consider the theory of the changes in θ which occur when ν_a and μ_a are comparable in magnitude, and when a retarding field for ions makes $\nu_p = \mu_p$.

The data of Figs. 23 and 24 show that if a clean filament is held at constant temperature in Cs vapor of a definite pressure, θ increases at first at the steady rate μ_a/σ_{A1} but thereafter the rate decreases until finally θ approaches a steady limiting value which we shall call θ_∞. Eq. (29), which applies to this case, may be written in the following form, since $\alpha_a = 1$

$$\sigma_{A1} d\theta/dt = \mu - \nu. \tag{38}$$

In this discussion we shall omit the subscripts of μ_a and ν_a except where necessary to prevent confusion.

Values of θ_∞

When $\theta = \theta_\infty$ we should have $\nu = \mu$. Thus, since by Eqs. (6) to (10) and the data of Table I, ν is given as a function of θ_n and T, we can calculate θ_n from μ and T. For each of the temperatures used in the ex-

[18] P. B. Moon, Proc. Camb. Phil. Soc., *27*, 570 (1931).

periments of Figs. 23 and 24 we have constructed, by the data of Table I, a curve giving ν as a function of θ_n in the range near θ_∞ and from this curve have read off the value of θ_n by taking $\nu = \alpha_o \mu_a$ as given by the steady ion current method. θ_∞ (by Eq. (12)) is then equal to $\theta_n + 0.005$. The horizontal portions of the full line curves in Figs. 23 and 24 have been drawn by using these calculated values of θ_∞. The close agreement of these horizontal lines with the limiting values of θ given by the experimental points is an illustration of the accuracy of our general equations for ν_a in terms of θ and T, and serves to justify our use of the surface phase postulate.

Calculation of transient curves

By expressing ν as a function of θ and T, we can, by integration of Eq. (38), theoretically obtain θ as a function of t. The experimental determinations of ν_a have shown that ν_a at constant T increases very rapidly with θ, so that within any narrow range of values of θ, say between θ_1 and θ_2, we may put

$$\nu = K \exp (H\theta), \tag{39}$$

where K and H are constants within the range θ_1 to θ_2, but depend on the values of θ_1 and θ_2. More strictly, we may define H by differentiation of Eq. (39)

$$H = d \ln \nu / d\theta. \tag{40}$$

In Fig. 25 the ordinates are values of H calculated in this way by differentiation of the expression we have derived for $\ln \nu_a$ as functions of θ and T. It is seen that except for very small and very large values of θ, H changes relatively slowly with θ, so that the use of Eq. (39) is justified if the range θ_1 to θ_2 is not very great.

Inspection of the experimental data of Fig. 24 shows that the transition between the sloping straight line ($\sigma = \mu t$) and the horizontal straight lines ($\theta = \theta_\infty$) is very rapid. Because of the large magnitude of H, a very small decrease in θ below θ_∞ lowers ν_a to a value which is negligible compared to μ, so that $d\theta/dt$ becomes constant. Thus, to calculate the whole curve, we need only to have an expression for ν which applies to a narrow range of θ.

Introducing the value of ν from Eq. (39) into Eq. (38), we find that the final steady value θ_∞ is given by

$$\nu = K \exp (H\theta_\infty) = \mu. \tag{41}$$

Case I. If we start with a completely coated filament at $t = 0$ we obtain by integration

$$\exp (-\mu H t/\sigma_{A1}) = 1 - \exp [-H(\theta - \theta_\infty)]. \tag{42}$$

Curves IV and V in Fig. 24 and curve IV in Fig. 23 are examples of Case I. For each point the completely coated filament was suddenly raised to the indicated temperatures by a condenser discharge and held there by the proper current.

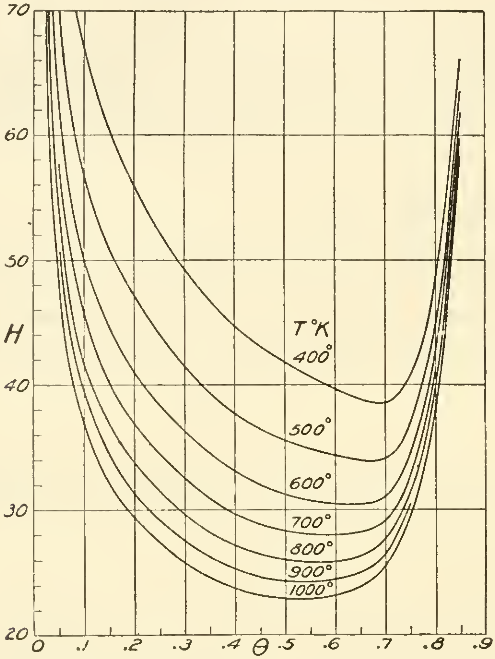

FIG. 25. Values of H, the relative rate of increase of ν_a with θ, defined by Eq. (40).

The full line curves IV and V in Fig. 24 were calculated accurately by Eq. (42), by using $\mu = 6.2 \times 10^{11}$, $\sigma_{A1} = 4.8 \times 10^{14}$, and for curve IV, $\theta_\infty = 0.72$, $H = 33.9$ at 530°, while for curve V, $\theta_\infty = 0.372$, $H = 30.4$ at 704°. For Fig. 23 (curve IV), $\theta_\infty = 0.056$ at 970°. As these values of θ_∞ were calculated from the values of μ, no adjustable parameters have been used in the construction of these curves.

Case II. Starting with $\theta = 0$ at $t = 0$ integration gives (if we neglect $\exp(-H\theta_\infty)$ compared to unity):

$$\exp(-\mu Ht/\sigma_{A1}) = \exp(-H\theta) - \exp(-H\theta_\infty). \tag{43}$$

The curve *OPNP′C* in Fig. 26 is the curve given by this equation. Except for a short transition region the curve nearly coincides with its two asymptotes *OA* and *BC*. It is therefore more convenient to express it in terms of the vertical displacement δ of a point P from the line OA or the displacement δ' from the horizontal line BC. If we let t_1 be the abscissa

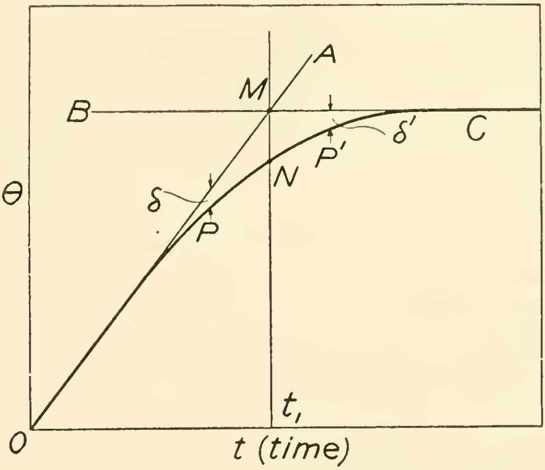

FIG. 26. Curve and construction describing Eqs. (43) to (45) used in calculation of transient curves.

corresponding to the intersection M of OA and BC, our equations become

$$\exp\,(H\delta) = 1 + \exp H\mu(t_1 - t)/\sigma_{A1} \tag{44}$$

and

$$\exp\,(H\delta') = 1 + \exp H\mu(t - t_1)/\sigma_{A1}. \tag{45}$$

Thus at points P and P', which are displaced from MN by equal horizontal distances, but in opposite directions, δ and δ' are equal. The slope of the tangent to the curve at N is one-half the slope of the line OA.

The full line curves which branch off from the lines I, II and III in Fig. 24 have been accurately calculated by these equations without the use of adjustable parameters.

The nearly perfect agreement of the points with the curves proves that the transient states during the condensation and evaporation of caesium atoms from these concentrated films are determined by the balance between the rates of condensation and evaporation as given by Eq. (38).

These experiments also prove that the surface phase postulate (S.P.P.) is applicable to these films. The agreement between the calculated curves and the experimental points shows that ν_a is determined by θ and T in accordance with Eqs. (6 to 10) and does not depend on the manner in which θ has been reached; i.e., by condensation or by evaporation.

In the transient experiments at low θ (Fig. 23) departures from the S.P.P. might be expected to occur. It has been shown that one-half percent of the surface of the filament consisted of "active spots." The final value of θ_n for 970° and $\mu_a = 6.2 \times 10^{11}$ (curve II) is calculated to be 0.051, but the plotted data show that in about 2 minutes a final value of 0.056 was reached, indicating that the active areas ($\theta = 0.005$) had been completely filled. Now in the transient state, as the filament is slowly coated, the concentrations in the normal and active areas would remain equal if there were no surface mobility by which the active areas could be filled. In 2 minutes the maximum value of θ (no reevaporation) which could be produced by the arriving atoms is $\backsim 0.16$. However, the active areas contribute only 1/200 of this or a θ of $\backsim 0.0008$ and without migration can be filled only after more than 12 minutes. It was particularly observed that the value of θ (0.056) reached in 2 minutes showed no increase after periods as long as 60 minutes. Also a cold filament nearly completely coated ($\theta \backsim 1.0$) when heated to 970° (curve IV) quickly attained the same final value of θ leaving no doubt as to the absence of any delay in reaching a steady value of θ. The full line branching curves in Fig. 23 calculated with the assumption of complete occupation of the active spots by migration early in the coating process, agree excellently with the observed points. The existence of an *interphase surface mobility* is thus well demonstrated. It is only by virtue of such mobility [15] that the S.P.P. applies to these experiments with dilute films.

Since the surface diffusion coefficient for these films is known [15] from other experiments, it has been possible [19] to calculate the distance which the adatoms may move in reaching active spots without disturbing the surface phase equilibrium. This distance ($\backsim$ 0.03 cm) was found to be large compared to the distance ($\backsim$ 0.001 cm) between active spots assuming these are located along crystal boundaries.

XII. MECHANISM OF CONDENSATION AND EVAPORATION FOR CONCENTRATED FILMS

The fact that $\alpha_a = 1$ up to values of θ as high as $\theta = 0.98$ is of profound significance in its bearing on possible mechanisms of condensation and evaporation.

According to the reversibility principle [20] "every element in the mechanism of a reversible process must itself be reversible," so that "the mechanism of evaporation must be the exact reverse of that of condensation even down to the smallest detail."

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[19] See reference 16, discussion of Eq. (12).

[20] I. Langmuir, *Jour. Amer. Chem. Soc., 38,* 2221–2295 (1916). See particularly page 2253 and footnote on page 2262.

Let us postulate several different possible mechanisms for evaporation and see whether or not, when they are reversed, they yield reasonable mechanisms for condensation and whether these are consistent with the experimental fact that $\alpha = 1$.

We first need to define some terms which will help to make our concepts more precise. In a state of equilibrium the atoms near a plane surface may be divided in general into four groups:

(1) *Adsorbed atoms or adatoms.* These are the atoms on the surface which contribute to θ.

(2) *Incident atoms,* or atoms which are moving towards the surface from remote regions. The paths described *by the nuclei* of such atoms are called *incident paths.*

(3) *Emergent atoms,* or atoms which are receding from the surface along paths (emergent paths) that will carry them to remote regions.

(4) *Hopping atoms,* or atoms whose nuclei describe paths (hopping paths) that originate and terminate on the surface.

We may define the *remote region* as that region which lies outside of the range of the surface forces, where the paths of the atoms are straight lines. The region closer to the surface where the paths are curved we shall call the *force sheath.*

When the nucleus of an incident, or a hopping atom, approaches to a definite point close to the original surface, the atom either becomes an adatom or it starts to describe a new path (emergent, or hopping). Let us call this definite point the *terminus of the path.* Similarly, each emergent and hopping path has an *origin.* The straight paths of the incident and emergent atoms in the remote region, if extended as straight lines to their intersections with an ideal plane at the adsorbing surface, give points which we shall call the *flight termini* and *flight origins.*

When equilibrium prevails, the concentration of atoms, their directions of motion, and their velocities are governed by the laws of the Maxwell-Boltzmann distribution (M.B.D.) throughout the force sheath as well as the remote region. Thus, all the paths (incident, emergent and hopping) that pass through any point have a spherically symmetrical distribution of directions at that point. The concentrations of atoms must vary in accord with the Boltzmann equation:

$$n = n_0 \exp\left(-Ve/kT\right), \tag{46}$$

where Ve is the increase in potential energy of an atom when it passes from a region where the concentration is n_0 to one at which it is n.

We see, then, that the flight termini and flight origins must be uniformly distributed over the ideal surface plane (i.e., distributed with uniform probability per unit area).

Since the adatoms are held by strong forces originating from the underlying tungsten atoms which are arranged in a definite surface lattice, there must be a strong tendency for the adatoms to occupy definite positions (elementary spaces) on the surface. Experiments on the mobility of caesium adatoms on tungsten[15] have shown that the activation energy needed to cause an adatom to hop from one elementary space to an adjacent one is about 0.6 electron-volts. Introducing this value into the exponent of Eq. (46) we find that at $T = 1000°$ the probability per unit volume for the occurrence of an atom (i.e., its nucleus) in the potential depression near the center of an elementary space is 1050 times as great as the corresponding probability for a position at the potential barrier which separates the elementary spaces.

Thus the adatoms are normally oscillating about equilibrium positions corresponding to the elementary spaces, with amplitudes which are rather small compared to the distance between elementary spaces, and only rarely hop from one position to another.

Evaporation of adatoms from dilute films

With the foregoing concept of elementary spaces, it might seem reasonable to postulate that most of the evaporating adatoms pass from their normal positions directly into the vapor phase as emergent atoms. If we think of the reverse process, however, we recognize that since the flight termini must be uniformly distributed over the surface, the incident atoms cannot in general have paths which lead them directly to the normal equilibrium positions. A large portion of the incident atoms must make their first contact with the surface in positions close to the potential barriers, and if $\alpha = 1$ all of these must then move to their final normal positions by a series of hops. Conversely, we must reason, by the reversibility principle, that a large fraction of the emergent atoms have flight origins near the potential barriers in spite of the low concentration of adatoms in these regions.

A little closer consideration shows that although at the barrier the concentration is only 1/1000th of that at the normal positions, this difference is counterbalanced by the fact that the probability of evaporation of any atom at the barrier is 1000 times as great as for an atom in a normal position. Thus the evaporation is essentially uniform over the surface, although the distribution of adatoms is nearly discontinuous.

It is thus evident, if $\alpha = 1$, that hopping paths must be enormously more numerous than emergent paths. Surface mobility is an essential part of the mechanism of evaporation.

Emergent atoms from nearly saturated films

Let us imagine a nearly saturated adsorbed film ($\theta \backsim 1$) from which adatoms pass as emergent atoms into the gas phase. If this is the only mechanism of evaporation, then condensation can occur only when incident atoms make their first contact with the surface in a vacant elementary space. All other incident atoms must be reflected; that is, they must escape again by emergent paths. Hopping paths would have to be excluded, for they would provide other opportunities for condensation, and therefore there would be other mechanisms for evaporation than those which we postulated as the only possible ones.

The probability that a flight terminus shall lie in a vacant space is $1 - \theta$. The probability that an incident atom should fly into a vacant space without colliding with adjacent atoms is very much less than $1 - \theta$. Thus, on the basis of our assumed mechanism, α would have to be less than $1 - \theta$.

An apparent reflection coefficient approaching unity for incident atoms striking a covered part of the surface may readily be accounted for by an extremely high evaporation rate from the 2nd layer of atoms as compared to that from the 1st layer.[21] It is reasonable to assume, however, that an atom cannot exist, even momentarily, in a 2nd layer unless it can be supported by four underlying adatoms in the 1st layer. The chance that a given space is occupied is θ and the chance that 4 given spaces are occupied is θ^4. Thus the probability that an incident atom will evaporate from the 2nd layer is θ^4 so that the apparent value of α would be $1 - \theta^4$. Experiments with steel balls thrown at random onto a surface partly covered (to the fraction θ) with similar balls, in random arrangement in spaces which form a square lattice, show that the fraction of incident balls which go into a second layer is, in fact, very close to θ^4, for values of θ from 0.2 to 1.0. Thus for $\theta = 0.85$, α would be 0.48 and for $\theta = 0.98$, $\alpha = 0.078$.

With this mechanism for condensation, most of the atoms which evaporate would have to make one or more collisions with the adjacent adatoms before they escape.

Although this postulated mechanism is probably suitable for the explanation of many cases of adsorption of gases on solids, it obviously is inapplicable to the case of caesium films on tungsten and all other cases in which $\alpha = 1$ up to high values of θ.

With high values of θ and α the emergent atoms must come from a second adsorbed layer

Since the paths of incident atoms cannot in general be directed towards regions in which the surface concentration is below the average, it must follow, if $\alpha = 1$, that just after condensation the concentration is locally raised at the point of condensation. Conversely, an atom can emerge only from regions having locally abnormally high surface concentrations and the act of emergence must bring the local surface concentration back to normal. It thus seems impossible to reconcile the observed simultaneous occurrence of high values of α and of θ with any mechanism by which an appreciable fraction of the emergent atoms have path origins in the first adsorbed layer, even if we assume a high mobility among the adatoms.

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[21] I. Langmuir, *Proc. Nat. Acad. Sci.*, *3*, 141 (1917).

These difficulties disappear, however, if we postulate that the origins of a large fraction of the emergent paths lie in a second adsorbed layer. We must assume that adatoms in the first layer hop, from time to time, up into a second layer which, however, covers only a very small fraction of the surface. The atoms in this second layer migrate over the surface and may evaporate or may hop back into vacant spaces in the first layer. Since an atom which evaporates from the dilute film of the second layer does not leave a "hole," no difficulty occurs in assuming that all incident atoms condense by the reverse process.

Covering fraction θ_2 in second layer

We have seen that the heat of evaporation (at constant pressure) of caesium adatoms from tungsten, for values of θ approaching unity, is about 41,000 calories per gram atom, which is equivalent at 1.78 electron-volts. This, of course, represents the energy that must be expended in taking an adatom from the first layer of adatoms out to a remote region.

An atom in a second layer is not in direct contact with the tungsten surface, but is in approximately the same condition as an atom on the surface of metallic caesium. The vapor pressure p of caesium is given (in baryes) by[1]

$$\log_{10} p = 10.65 - 3992/T. \tag{47}$$

The heat of evaporation corresponding to this equation is 18,240 calories or 0.79 volt, or only 44 percent of that of adatoms in the first layer.

The average "evaporation life" of an atom[22] in the surface of a solid or liquid is given by

$$\tau = (2\pi mkT)^{\frac{1}{2}}\sigma_1/p, \tag{48}$$

where τ may be defined by the statement that dt/τ is the probability that any surface atom will evaporate in the time dt. Placing $\sigma_1 = 3.56 \times 10^{14}$ we thus find that for Cs atoms in the temperature range from $T = 300$ to $1100°$, τ is given in seconds by

$$\log_{10} \tau = -12.82 + 3840/T. \tag{49}$$

[22] See Eq. (15), reference 2.

Let us now assume provisionally that τ is the same for all exposed adsorbed atoms in the 2nd (or 3rd) layer on tungsten as for atoms in a surface of metallic caesium at the same temperature. We thus take τ to be independent of the surface concentration of atoms although for the 1st adsorbed layer on tungsten the strong repulsive dipole forces between adatoms cause τ to decrease as θ_1 increases. Since Cs atoms on a layer already covered by caesium probably have very small dipole moments, and any small moment that does exist may be compensated for by attractive forces, it seems reasonable to make this simplifying assumption.

We may then put

$$\tau = \sigma_1 \theta_2 / \nu \tag{50}$$

and under steady conditions in which $\nu = \mu$ we then have from Eq. (49)

$$\log_{10} (\mu/\theta_2) = 27.37 - 3840/T. \tag{51}$$

Here θ_2 represents the fraction of the available part $(\theta_1{}^4)$ of the first layer which is covered by the adatoms in the second layer. The total number of atoms in the second layer per unit area of true tungsten surface is thus $\sigma_1 \theta_1{}^4 \theta_2$.

When μ increases to the value μ_2 corresponding to saturated vapor at the temperature of the filament, θ_2 must rise to unity. Thus by Eq. (51) we have an equivalent definition of θ_2

$$\theta_2 = \mu/\mu_2. \tag{52}$$

In experiments on transients μ or ν must have values which give reasonable time intervals for coating or depleting the surface. With $\mu = 10^{11}$ the coating time to $\theta = 1$ is one hour and with 10^{15} it is 0.4 second. Let us therefore choose these values of μ and calculate by Eq. (6) for various values of θ_n the corresponding temperatures. These data are given under T in Table V.

With these values of T, putting $\nu = \mu$ we calculate by Eq. (51) the values of θ_2 given in Table V. The values of T in the lowest line are those obtained from Eq. (51) by putting $\theta_2 = 1$; these are the temperatures at which liquid caesium (polyatomic layers) would condense on the filament.

Examination of these data shows that $\theta_1{}^4\theta_2$, the number of caesium atoms per unit area in the second layer needed to give an evaporation rate equal to μ is extremely small until θ_1 reaches values of about 0.96. For still higher values of θ_1, θ_2 increases rapidly. When θ_2 becomes comparable with unit, we must take into account the adsorption in the third and higher layers.

TABLE V

Covering Fractions θ_1 and θ_2 for the First and Second Layers and Rates of Interchange ρ of Atoms Between These Layers

				$\mu = 10^{11}$			$\mu = 10^{15}$	
θ_n	θ_1	θ_1^4	T°K	θ_2	ρ	T°K	θ_2	ρ
0.5	0.505	0.065	605	9.5×10^{-11}	1.3×10^{17}	789	3.2×10^{-8}	5.6×10^{19}
0.7	.705	.24	516	1.2×10^{-9}	8.4×10^{17}	661	2.8×10^{-7}	2.5×10^{20}
0.9	.905	.67	407	1.2×10^{-7}	1.6×10^{19}	498	2.2×10^{-5}	4.6×10^{21}
0.95	.955	.83	332	1.5×10^{-5}	4.1×10^{20}	391	3.0×10^{-3}	1.7×10^{23}
0.96	.965	.89	306	1.6×10^{-4}	2.1×10^{21}	355	2.8×10^{-2}	8.4×10^{23}
0.97	.975	.91	270	6.9×10^{-3}	2.8×10^{22}	308	—	—
			234	1		310	1	—

Polyatomic layers with nearly saturated vapor

A mathematical theory of the building up of polyatomic adsorbed layers as the vapor approaches saturation has already been given.[23] This theory should now be modified by assuming that adsorption of an atom in the *n*th layer can occur only on an underlying group of at least 4 atoms in the $(n-1)$st layer. A rough estimate of the number of atoms in each layer may be made by assuming that the number of atoms in the successive layers decreases in the ratio $1:\theta_2^4$. Thus σ, the total number of atoms adsorbed (in all layers) per unit area of the filament surface, is

$$\theta=\sigma/\sigma_1=[\theta^1+\theta_1^4\theta_2(1+\theta_2^4+\theta_2^8+\cdots)]$$

or $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (53)

$$\theta=[\theta_1+\theta_1^4\theta_2/(1-\theta_2^4)].$$

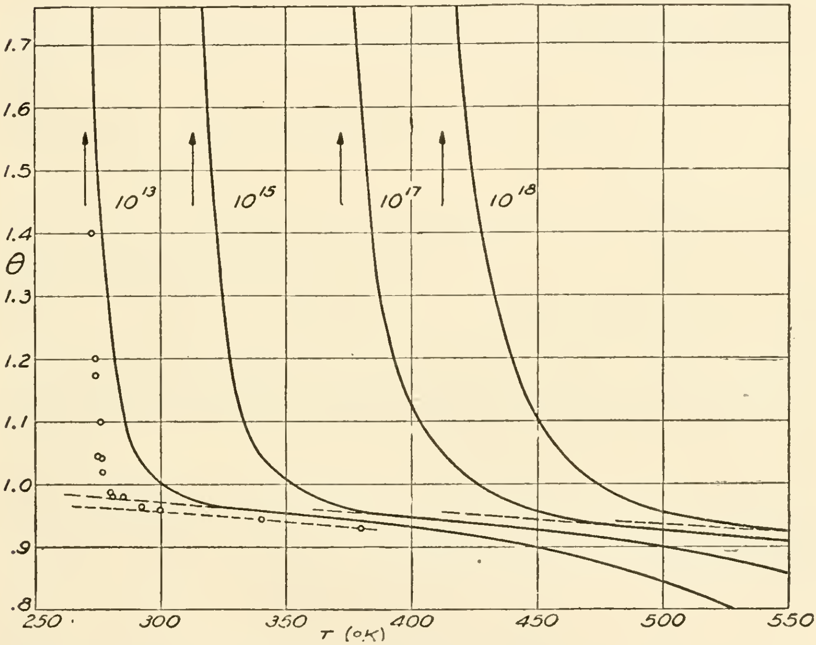

FIG. 27. Formation of a second layer of Cs atoms (calculated by Eqs. (6) and (53)) for different values of μ_a. Arrows give temperature corresponding to saturated Cs vapor. Circles give experimental data obtained at $\mu_a = 10^{13}$.

The rapidly rising portions of the curves in Fig. 10 near $\theta = 0.95$ have been calculated by this equation with values of θ_1 and θ_2 obtained from Eqs. (6) to (10) and (51).

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[23] I. Langmuir, *Jour. Amer. Chem. Soc., 60,* 1374 (1918).

With the bulb containing saturated caesium vapor at a temperature T_s, θ does not exceed unity until the filament temperature T is lowered to within 25° of T_s for $\mu = 10^{11}$ (or 80° for $\mu = 10^{18}$). When $T - T_s$ is 8° (or 24°), θ_2 is 0.3 so that 30 percent of the surface is covered by a second layer of atoms although 2 percent (or 5 per cent) of the tungsten surface is still bare (due to repulsive forces in this layer). There are then only enough atoms in the 3rd layer to cover 0.007 of the surface. When $T - T_s$ is 0.6° for $\mu = 10^{11}$ (or 1.9° for $\mu = 10^{18}$) θ_2 is 0.9 so that the covering fractions for the successive layers are roughly 0.98, 0.77, 0.33, 0.14, 0.06, 0.026, etc., the total value of σ/σ_1 being about 2.3.

Experimental test of the formation of polyatomic layers

Fig. 27 shows the building up of a second layer of caesium atoms according to Eq. (53), for various values of μ. The vertical arrows represent the temperatures corresponding to saturated caesium vapor.

It was thought desirable to test for this formation of a second layer. At $\mu_a = 10^{13}$ filament A was maintained, either by passage of small currents or by radiation from filament B, at various temperatures slightly above $T_{\text{sat.}}$ (270°). The temperatures were computed from the measured resistance of the filament.

The adsorbed atom concentration at each temperature was measured by the two filament method. The circles in Fig. 27 give the experimental results. It was found that as indicated by the theory θ increased only slowly until a temperature within 20° of $T_{\text{sat.}}$ was reached. The increase up to this point was closely that given by Eq. (6) for atom evaporation in the first layer.[24] At $\sim$ 293° a much more rapid rise set in until at 273° a total θ of 1.4 was reached. The direction of the deviation from the theoretical curve shows that atoms evaporate more easily from the 2nd layer of Cs on tungsten than from metallic caesium. Since θ depends on the probability of evaporation of the adsorbed atoms in the 2nd layer, application of the Boltzmann equation serves to indicate the amount by which the heat of evaporation differs from that of liquid Cs.

$$n/n' = \exp\left(\Delta Ve/kT\right),$$

where n and n' are the theoretical and observed concentrations. Since n/n' is approximately 6 between 275° and 295°, $\Delta V \simeq 0.045$ volt. Thus the theory is extraordinarily well confirmed. There is no tendency to form a second layer until near $T_{\text{sat.}}$. Atoms adsorbed in the second layer are not held by forces at all approaching in magnitude those holding Cs directly to tungsten; since ΔV for metallic caesium and Cs adsorbed on tungsten in the first layer is almost 1 volt. The heat of evaporation from the second layer is even less than that from metallic caesium. All this is striking evidence of the true monatomic nature of the first layer of Cs on tungsten.

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[24] This behavior of θ near 1.0 makes it likely that σ_{A1} is more closely 4.9×10^{14} than 4.8×10^{14} as given by the previous less detailed experiments of Section V, introducing a possible error of about 2 percent in the calculations of θ.

Mobility and surface diffusion coefficient of adatoms

Let us consider σ adatoms per unit area distributed at random among elementary spaces which are arranged in a square surface lattice, each elementary space being a square of side a so that $a^2 = 1/\sigma_1$. Let τ be the average life of an adatom in a particular space when the 4 adjacent spaces are vacant. The probability per second that an atom in a given space will hop into a given adjacent vacant space is $1/4\tau$. We may take the probability of hopping into an occupied space to be zero. If we may assume that the atoms exert no appreciable forces on one another (except that needed to keep 2 out of a single space), τ may be taken to be independent of σ.

The flux φ of atoms per cm of length across a line midway between two adjacent rows (A and B) of elementary spaces (perpendicular to X axis) is

$$\varphi_{AB} = (a\sigma_A/4\tau)(1-\sigma_B/\sigma_1) \quad \text{from } A \text{ to } B$$

and

$$\varphi_{BA} = (a\sigma_B/4\tau)(1-\sigma_A/\sigma_1) \quad \text{from } B \text{ to } A. \tag{54}$$

The net flux or drift flux φ_D is thus

$$\varphi_D = (a/4\tau)(\sigma_A - \sigma_B) = (a^2/4\tau)d\sigma/dx. \tag{55}$$

The surface diffusion coefficient D may be defined by equating φ_D to $D\, d\sigma/dx$ and thus we find for all values of θ from 0 to 1

$$D = a^2/4\tau = 1/4\sigma_1\tau. \tag{56}$$

In case we have to deal with a hexagonal surface lattice in which atoms may hop to any one of six adjacent spaces, this equation needs to be modified merely by replacing the 4 in the denominator by 3. For tungsten surfaces which have been highly heated, the atoms are arranged in a surface lattice in which the elementary rectangle of dimensions 3.15 × 4.46A has one atom at each corner and one atom in the center. Each surface atom has thus 4 near neighbors and therefore Eq. (56) should be applicable.

This equation has been derived on the assumption that the time τ during which an atom remains in an elementary space is large compared to a/v, the time required for the passage of an atom from one space to the next.

When the time of transit a/v is not negligible, Eq. (56) needs to be modified merely by adding a/v to τ so that

$$D = a^2/4(\tau + a/v_2), \tag{57}$$

where v_2 the average velocity parallel to the plane of the surface (2-dimensional velocity) is given in cm sec.$^{-1}$ by

$$v_2 = (\pi kT/2m)^{\frac{1}{2}} = 11{,}428(T/M)^{\frac{1}{2}}, \tag{58}$$

M being the molecular or atomic weight.

If τ is negligible compared to a/v_2, this reduces to

$$D = (1/4)av_2. \tag{59}$$

In the elementary kinetic theory of gases it is shown [25] that the coefficient of self-diffusion of a gas is $D = (1/3)\lambda_3 v_3$ where v_3 is the average (3-dimensional) molecular velocity and λ_3 is the 3-dimensional free path. A similar calculation for the 2-dimensional case of surface diffusion leads to

$$D = (1/2)\lambda_2 v_2, \tag{60}$$

where λ_2 is now the length of the projection of the free path on the plane of the surface. If we identify λ_2 with a, this equation is the same as Eq. (59) except for the numerical factor. This difference is due to the fact that in deriving Eq. (60) it was assumed that all directions of motion in the plane are equally probable, while for Eq. (59) the motions were taken to be parallel to the two axes of the square lattice.

Measurements of the surface diffusion coefficient D_1 for Cs adatoms on tungsten for an average value of θ of about 0.03 have given,[15] for the temperature range from 650 to 812° K.,

$$\log_{10} D_1 = -0.70 - 3060/T. \tag{61}$$

Since the number of tungsten atoms per cm^2 on a tungsten surface is 1.425×10^{15} we must take this to be the number of elementary spaces and thus get

$$a_1 = 2.64 \times 10^{-8} \text{ cm}. \tag{62}$$

Using this value of a_1 and the value of v_2 from Eq. (58) we calculate τ_1 at various temperatures in the range from 650 to 812° and find that they are represented by

$$\log_{10} \tau_1 = -15.09 + 3082/T. \tag{63}$$

[25] See for example *Dynamical Theory of Gases,* J. H. Jeans, p. 326, Cambridge, 2nd Edition.

Values of τ_1 and D_1 (for Cs atoms in the 1st layer) are given for several temperatures in the 3rd and 2nd columns of Table VI.

TABLE VI

SURFACE DIFFUSION COEFFICIENTS FOR Cs ADATOMS IN 1ST AND 2ND LAYERS

τ_1 and τ_2 are the "lives" in elementary spaces in 1st and 2nd layers as given by Eqs. (63) and (64); τ is the "evaporation life" in 2nd layer given by Eq. (49).

T	D_1(cm² sec.⁻¹)	τ_1(sec.)	τ_2	a_2/v_2	D_2	τ
			$\times 10^{-14}$	$\times 10^{-14}$		
300	1.2×10^{-11}	1.5×10^{-5}	175.	31.	0.00034	0.95
400	4.3×10^{-9}	4.1×10^{-8}	26.	27.	.00134	5.9×10^{-4}
500	1.5×10^{-7}	1.2×10^{-9}	8.1	24.	.0022	7.2×10^{-6}
600	1.6×10^{-6}	1.1×10^{-10}	3.8	22.	.0027	3.8×10^{-7}
700	$8. \times 10^{-6}$	2.1×10^{-11}	2.2	20.	.0032	4.6×10^{-8}

The mobility of adatoms in the 2nd layer must be much greater than that in the 1st layer since the atoms in the 2nd layer are held by much weaker forces. For low values of θ_1 at which D_1 was measured, the heat of evaporation of atoms from the 1st layer is 2.83 volts. The potential barrier corresponding to the coefficient of $1/T$ in Eq. (63), 3082, is, as we have seen, 0.61 volt which is 21.5 percent of the heat of evaporation. The potential barrier separating the elementary spaces for the 2nd layer must be much less than 0.61 volt which is 78 percent of the heat of evaporation (0.79 volt) from the 2nd layer. It seems reasonable to assume that the barrier in this case also is approximately 21.5 percent of the heat of evaporation. This would give 0.17 volt. The Cs atoms in the 1st layer, however, because of their larger size compared to W atoms, constitute a rougher support for the atoms in the 2nd layer than is provided for the 1st layer of atoms by the underlying tungsten surface. Thus we may adopt the rough value 0.2 volt as most probable value for the barrier in the 2nd layer. This corresponds to a coefficient 1000 for $1/T$. This gives for the life τ_2 of an adatom in an elementary space of the 2nd layer

$$\log_{10} \tau_2 = -15.09 + 1000/T. \qquad (64)$$

We have taken the term -15.09 to be the same as in Eq. (63), since for evaporation [26] and for diffusion [27] this term remains nearly constant even for different substances.

Thus a general equation for the evaporation life τ was found [26] to be

$$\tau = 4.7 \times 10^{-27} M^{\frac{1}{2}} \sigma_1 T^{-1} \epsilon^{b/T}. \qquad (65)$$

Because of the similarity of the processes of evaporation and of mobility, by which atoms hop from one position to another, we may expect this

[26] Reference 2. See particularly Eq. (37) on page 2806.

[27] S. Dushman and I. Langmuir, *Phys. Rev.*, *20*, 113 (1922).

equation to be at least roughly applicable to surface diffusion. Putting $M = 133$, $\sigma_1 = 3.56 \times 10^{14}$ and $T = 500$ (the mean temperature) we find from Eq. (65)

$$\log_{10} \tau = -13.4 + 0.43b/T. \tag{66}$$

The values of τ_2 calculated from this equation by putting $0.43b = 1000$ are of roughly the same magnitude as those by Eq. (64). A change of about 10 percent in the assumed value of the coefficient of $1/T$ would bring the two equations into agreement at a given temperature.

The values of τ_2 calculated from Eq. (64) are given in the 4th column of Table VI, and D_2 calculated from these by Eq. (57) taking

$$a_2 = 5.3 \times 10^{-8} \tag{67}$$

is given in the 6th column while the time of transit a_2/v_2 is given in the 5th column.

The last column of Table VI gives the evaporation life of adatoms in the 2nd layer as calculated from Eq. (49). Comparing τ with τ_2 and a_2/v_2 we see that at $T = 300$ each adatom in the 2nd layer moves through about 10^{12} elementary spaces before evaporating and even at 700° it moves through 10^5 spaces during its life. This fact affords a simple explanation of the high values of α.

Surface random flux

A very useful concept[28] in the study of electric discharges in gases is that of random current density I_e. If n is the number of electrons per unit volume in a uniform plasma and v is their average velocity, then across any imaginary plane there is a current density $I_e = (1/4)nve$ of electrons which pass across the plane from one side to the other and an equal current of electrons passing back in the opposite direction.

Similarly for the motions of adatoms on any surface in a steady state we may define the *random flux density* φ as the number of atoms per unit length which cross any imaginary line in the surface from one side to the other (while an equal flux passes in the opposite direction).

If the adatoms move in random directions parallel to the plane of the surface with the average velocity v, then one-half the atoms on one side of the line are approaching the line with an average velocity $(2/\pi)v$. Thus we find

$$\varphi = (1/\pi)\sigma v = (\sigma_1/\pi)\theta v. \tag{68}$$

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[28] I. Langmuir and H. Mott-Smith, *G. E. Rev.*, *27*, 449 (1924); I. Langmuir and K. T. Compton, *Rev. Mod. Phys.*, *3*, 221 (1931)

If the adatoms, instead of moving with uniform velocity, hop from space to space as postulated in the derivation of Eqs. (54), (55) and (57), we obtain

$$\varphi = a\sigma_1\theta(1-\theta)/4(\tau + a/v_2) = (\sigma_1 D/a)\theta(1-\theta). \tag{69}$$

Rate of interchange of atoms between the first and second adsorbed layers

Consider that the first layer in a square surface lattice is nearly completely filled by adatoms as indicated in Fig. 28, so that the $\sigma_1(1-\theta_1)$ vacant spaces per unit area are separated from one another. The available elementary spaces in the second layer are indicated in the figure by crosses. Each vacant space in the first layer causes a decrease of four in the number of available spaces in the second layer; this number per unit of filament surface is therefore $\sigma_1[1-4(1-\theta_1)]$, which for values of θ_1 close to unity agrees with $\sigma_1\theta_1^4$ as deduced previously.

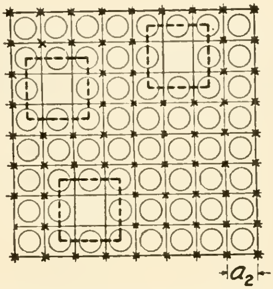

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Fig. 28. First layer in a square surface lattice nearly completely filled by adatoms, denoted by circles. Available spaces in the second layer are indicated by crosses.

Any adatom in the second layer which migrates across the dotted line in Fig. 28, which has a perimeter $8a_2$, evidently falls into the vacant space in the first layer. Thus the rate ρ at which atoms pass from the second to the first layer, expressed in atoms cm^{-2} sec.$^{-1}$, is

$$\rho = 8a_2\varphi_2\sigma_1(1-\theta_1). \tag{70}$$

Under equilibruim conditions this must be balanced by the passage of an equal number of atoms from the 1st and the 2nd layers. Thus ρ may be termed the *rate* of *interchange* between the 2 layers. If this rate is very high compared to the rates of evaporation ν or condensation μ from or to the surface, the relative numbers of adatoms in the two layers $\sigma_1\theta_1$ and $\sigma_1\theta_2\theta_1^4$ will be the same whether or not the adsorbed films are in equilibrium with the vapor phase. Therefore the conditions for which the surface phase postulate will be fulfilled are $\rho/\nu \gg 1$, and $\rho/\mu \gg 1$.

In deriving Eq. (70) we considered the rate at which atoms in the 2nd layer move to and drop into holes in the 1st layer. It is, however, possible, because of the mobility in the 1st layer, for holes in the 1st layer to move to atoms in the 2nd layer. Considerations like those used in deriving Eq. (69) lead to the conclusion that the diffusion coefficient for *holes* is the same as for *atoms* and that the surface flux of holes as well as that of atoms is given by the last member of Eq. (69). Taking Eq. (70), after eliminating φ_2 by Eq. (69),

$$\rho = 8\sigma_1^2(D_2 + \theta_1 D_1)(1-\theta_1)\theta_2(1-\theta_2). \tag{71}$$

The values of ρ given in Table V were obtained by this equation, with the data for D_2 given by Table VI. They are large compared with μ or ν and therefore the surface phase postulate applies.

Chapter Seventeen

THE MOBILITY OF CAESIUM ATOMS ADSORBED ON TUNGSTEN

A HEATED tungsten filament in presence of Cs vapor adsorbs Cs atoms. The number of atoms per unit area, σ, can be measured (if $\sigma < 3.6 \times 10^{13}\ \mathrm{cm}^{-2}$) by suddenly heating the filament (surrounded by a negatively charged cylinder) and observing the ballistic kick on a galvanometer, since every atom escapes as a positive ion.

Three cylinders placed end to end surrounded a straight filament. With all three cylinders at positive potential (22 volts) a Cs film was formed with the filament at low temperature. The Cs vapor was then frozen out by immersing the bulb in liquid air. The filament was next heated to a temperature (848° K.) at which σ was reduced below 3.6×10^{13} and the temperature was then lowered to T_1 at which the rate of evaporation of atoms was very low. The potential of the central cylinder was then changed to -22 volts leaving the other two at $+22$. This allowed the Cs on the central part of the filament to escape as ions. The current to this central cylinder gave the rate of evaporation. After the removal was nearly complete, the potential of the central cylinder was altered to -44 volts and because the accelerating field for ions then reached into the end cylinders, an additional length a was freed from Cs. The current-time integral permitted the total length of cleaned filament to be measured.

In this way a *standard* Cs *distribution* was obtained in which the central part, free from Cs, extended at each end a distance of 0.165 cm into the end cylinders, while the two end sections were uniformly coated with Cs to a concentration of $\sigma = 2.73 \times 10^{13}$.

With the filament in this standard condition the temperature was changed to T_2 for a time t_2 while all three cylinders were at $+22$ volts so that no ions could evaporate. T_2 was chosen so low ($<848°$) that there was no appreciable change in σ by atom evaporation during the time t_2. During this time, however, the Cs migrated to some extent from the end sections into the central section. The number of atoms which had arrived were then measured by flashing the filament while the three cylinders were put at -22 volts, but the current to the central cylinder only was measured.

The migration of the Cs may be looked upon as a surface diffusion, the number of atoms per unit time crossing each unit of length of a line on the surface being $Dd\sigma/dt$. Treating the problem as one of diffusion, assuming as usual that D is independent of σ, it is then possible to calculate D from the foregoing experiments.

Measurements of the migration were made at $T_2 = 654°$, $702°$, $746°$, and $812°$ K. with times from 200 to 4000 seconds. At each temperature the values of D obtained were approximately independent of t_2 (slight increase with t_2). The values of log D plotted against $1/T$ gave a straight line so that

$$\log_{10} D = -0.70 - 3060/T. \qquad (1)$$

At 812° this corresponds to $D = 3.4 \times 10^{-5}$ cm^2 sec.$^{-1}$.

A few experiments were made in which the Cs concentration on the end sections in the standard condition was altered to 1.74×10^{13}. At 812° a value of D of 1.4×10^{-5} was found. Thus D varies considerably with σ so that the experiments have given as yet only a kind of average value of D over the range from $\sigma_{\max}$ to 0.

Determinations of D at higher concentrations have been made by another method. In presence of a given pressure of Cs, the Cs film on a filament at about 1000° K. surrounded by a negatively charged cylinder can exist in two phases, separated by a definite boundary. From the more concentrated phase (α phase) Cs evaporates as atoms while from the dilute β phase Cs evaporates as ions; both of these rates being equal to the rate of arrival from the vapor phase. At a given filament temperature there is only one pressure p_0 at which these two phases can coexist. If the pressure is changed to p_1 the phase boundary moves with a definite velocity v along the length of the filament, causing either one or the other phase to disappear.

At the phase boundary there is a sharp concentration gradient. The resulting surface migration is balanced by differences between the rates of evaporation into and arrival from the vapor. The rates of evaporation of atoms and ions, ν_a and ν_p, both depend on T and σ, but the rate of condensation μ is fixed by the Cs vapor pressure. The total evaporation rate $\nu = \nu_a + \nu_p$ rises from 0 at $\sigma = 0$ to a maximum at about $\sigma = 7 \times 10^{12}$, falls to a minimum at 43×10^{12} and then rises indefinitely. The curve $\nu - \mu$ as a function of σ thus intersects the σ axis at three points and forms two closed areas A_1 and A_2, enclosed by the curve and the σ axis. A recent article,[1] gives data from which such curves can be prepared. Mathematical analysis shows that the condition for a stationary phase boundary is that $A_1 = A_2$.

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[1] I. Langmuir, *Jour. Amer. Chem. Soc., 54,* 1252 (1932).

If at any temperature the rate of arrival of Cs is changed from μ_0 to μ_1, the velocity of the movement of the boundary is given by

$$v = (D/2A)^{1/2}(\mu_1 - \mu_0)$$

This was derived on the assumption that D is independent of σ and that v is small.

The experiments show in fact that $A_1 = A_2$ and that v varies in proportion to $\mu_1 - \mu_0$. From measurements at 967° K. a value of $D = 6 \times 10^{-4}$ was obtained. The concentration of the α phase was 7.3×10^{13}. From Eq. (1) for this temperature we calculate $D = 1.1 \times 10^{-4}$. The higher concentration is the probable reason for the higher observed value of D by this method.

The strong repulsive forces between the adatoms explains the variation of D with σ. It is planned to develop a quantitative theory of this effect. The coefficient of the last term of Eq. (1) corresponds to an activation energy for diffusion amounting to 0.61 volt. The atoms are normally held in definite positions with respect to the underlying tungsten lattice, but by acquiring thermal energy of agitation of 0.61 volt or more, may hop into adjacent vacant spaces. With definite knowledge of the lattice and the forces acting on the atom, it is hoped that the average life τ in each elementary space may be determined.

Chapter Eighteen

TYPES OF VALENCE

From the theory proposed by G. N. Lewis in 1916 and subsequently extended by the writer, it is clear [1] that the term valence has been used in the past to cover what we may now recognize as three distinct types of valence, viz.:

1. Positive valence: the number of electrons an atom can give up.
2. Negative valence: the number of electrons an atom can take up.
3. Covalence: the number of pairs of electrons an atom can share with its neighbors.

It was shown that these fundamental conceptions of valence as well as the actual numerical values of each type of valence for most of the elements could be derived from a few postulates regarding the structure of atoms. The following method of deriving these relationships, however, is not only much simpler than that previously given by the writer, but throws a new light on the relationships between the different types of valence.

We will take for granted the Rutherford type of atom, which consists of a positive nucleus surrounded by a number of electrons equal to the atomic number of the atom. We will also assume that Coulomb's law applies to the forces between the charged particles in the atom, but at the same time will recognize the existence of repulsive forces in atoms which prevent the electrons from falling into the nucleus. For the present purpose, however, it is immaterial whether the repulsive force is a dynamic force (centrifugal force) such as that assumed by Bohr, or is a static force as postulated by G. N. Lewis, J. J. Thomson or recently by the writer.[2]

We shall need to make only 3 postulates in regard to the structure of atoms, and these are consistent with those previously proposed.

Postulate 1.—The electrons in atoms tend to surround the nucleus in successive layers containing 2, 8, 8, 18, 18 and 32 electrons respectively.

The word atom is used in the broader sense which includes charged atoms (ions). If the number of electrons in an atom is such that they can not all form into *complete layers* in accord with Postulate 1, the extra electrons remain in the outside layer as an *incomplete layer* which we may designate as the *sheath* of the atom. Every electrically neutral atom must contain a number of electrons equal to the atomic number of the nucleus. If the outside layer of such an atom is nearly complete, the tendency expressed by Postulate 1 may cause a few additional electrons to be taken up in order to complete the layer, thus forming a negatively charged atom or ion. In such a case we may say that the sheath has been completed.

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[1] I. Langmuir, *Jour. Amer. Chem. Soc., 41,* 926 (1919), and *Jour. Ind. Eng. Chem., 12,* 386 (1920).

[2] *Science, 53,* 290, Mar. 25, 1921.

In the following discussion it is important to keep in mind this distinction between sheath and outside layer. Every incomplete outside layer which occurs normally is a sheath, but a complete outside layer may or may not be a sheath. The following definition will make this clearer. *The sheath of any atom (or atomic ion) consists of all the electrons in the outside layer provided that this layer is incomplete when the atom is electrically neutral.* Thus atoms of the inert gases (neon, argon, etc.) and ions such as Na^+, Ca^{++}, etc., have *no sheaths* for the outside layers of these atoms consist of electrons which already form a complete layer in the neutral atom. The sodium *atom,* however, has an *incomplete sheath containing* one electron, while the fluorine atom has an incomplete sheath of 7 electrons. The fluorine *ion,* on the other hand, has a *complete sheath* of 8 electrons.

The inert gases are the only elements whose neutral atoms have no sheaths, or in other words have all their electrons arranged in complete layers in accordance with Postulate 1. In all other atoms, the tendency expressed by this postulate can only be satisfied by an interaction between atoms involving a rearrangement of the electrons. This is to be regarded as the fundamental cause of chemical action and it is by such interaction that chemical compounds are formed.

When as the result of such rearrangement of electrons, the sheath of an atom has become complete, we may speak of the atom as a *complete atom.* Similarly if the interaction between atoms leads to complete satisfaction of the tendency of Postulate 1, so that all the atoms become complete, we may say that a *complete compound* is formed. We shall see that there are some factors which may oppose the formation of complete atoms and counteract the tendency of Postulate 1. In such cases incomplete atoms and compounds may result.

According to Postulate 1, the first complete layer in any atom consists of two electrons close to the nucleus. Let us call this stable pair of electrons a *duplet* and let us broaden the definition of duplet to include any pair of electrons which is rendered stable by its proximity to one or more positive charges. We may now state the second postulate.

Postulate 2.—Two atoms may be coupled together by one or more duplets held in common by the completed sheaths of the atoms.

Let us now analyze the conditions that must be fulfilled if the interaction between atoms is to result in the formation of a complete compound.

A given group of neutral atoms may interact to complete their sheaths in two ways:

1. *By transfer of electrons.*
    - *a.* Atoms having sheaths containing only a few electrons may give up these extra electrons to other atoms.
    - *b.* Atoms having nearly complete sheaths may take up electrons from other atoms.
2. *By sharing duplets.*
   Atoms may share duplets with other atoms (Postulate 2) and thus complete their sheaths with fewer electrons than would otherwise be necessary.

Let e be the number of electrons in the sheath of any neutral atom and let s be the number of electrons in the sheath after the atom has interacted with others. For the atoms of any complete compound the values of s can be only 0, 2, 8, 18 or 32.

In any group of atoms, the only electrons available for the formation of the complete sheaths are those which originally form the incomplete sheaths. The number of such electrons, $\Sigma(e)$, is found by adding the values of e for the individual atoms. In the resulting compound, if no duplets are shared by the atoms, the total number of electrons in the complete sheaths is $\Sigma(s)$. Every duplet held in common by two atoms, however, decreases by two the number of electrons required to form the sheaths. If then we let B be the total number of duplets shared within the given group of atoms, the number of electrons in the completed sheaths of the atoms of the compound is $\Sigma(s)-2B$. Since this must equal the number in the original neutral atoms, we have the relation[3]

$$\Sigma(e)=\Sigma(s)-2B. \qquad (1)$$

This is the condition for the formation of a complete compound. We shall now proceed to put this equation into a simpler form and one which has more significance to the chemist.

The transfer of electrons that may occur during the interaction between atoms corresponds to what has been called positive and negative valence while the sharing of duplets corresponds to covalence. We shall see that the positive and negative valence differ from one another fundamentally only in algebraic sign, so that we shall find it convenient to include both positive and negative valence under the term *electrovalence,* which we may designate by the symbol v_e. We shall then adopt the convention that the electrovalence of an atom is positive when the atom gives up electrons and negative when it takes up electrons. The *electrovalence* of an atom in any compound may thus be defined as the number of electrons which the neutral atom must give up in forming that compound. If the neutral atom must *take up* electrons, the electrovalence is expressed as a negative number. The electrovalence of any atom is thus given by the expression

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[3] Equation (1) is a more general statement of the relation $e = 8n - 2p$ which has been used previously by the writer in discussing the "octet theory."

$$v_e = e - s. \qquad (2)$$

Electropositive atoms in complete compounds lose all the electrons in their sheaths so that s is zero and therefore v_e is positive and equal to e. For electronegative atoms s is always greater than e so that v_e is negative.

Let us define the *covalence* (v_c) of an atom as the number of duplets which that atom shares with neighboring atoms. Every duplet shared by two atoms corresponds to a (covalence) *bond* between atoms, and we have already represented the number of such bonds in a given group of atoms by the symbol B. If we now form $\Sigma(v_c)$ by adding the values of v_c for all the atoms in the given group, we count each bond twice. Hence we may place

$$\Sigma v_c = 2B. \qquad (3)$$

By substituting (3) and (2) in (1) and rearranging terms we find

$$\Sigma v_e + \Sigma v_c = 0. \qquad (4)$$

This simple result may be stated as follows:

The sum of the electrovalences and covalences for all the atoms in any complete compound is zero.

Electrovalence and covalence are thus in a sense supplementary to one another. If we represent $v_e + v_c$ by v, Equation 4 takes the form

$$\Sigma v = 0 \qquad (5)$$

for any complete compound, and this suggests that the quantity v may have some simple physical significance.

In accordance with the nomenclature introduced by Lewis we may define the *kernel* of an atom as that part of an atom which remains after the sheath is removed. Since the neon atom has no sheath the whole atom constitutes a kernel with zero charge. The kernel of the sodium atom is the sodium ion with single positive charge, while the kernel of the fluorine atom (or fluorine ion) consists of the nucleus and two electrons, the whole having 7 positive charges.

Since the sheath of any neutral atom consists of e electrons, the positive charge on the kernel is also e. In any complete atom there are s electrons in the sheath. When the atom does not share duplets with other atoms (covalence zero) then the total charge of the atom is $e - s$. If, however, any two atoms hold a duplet in common the total charge of the two atoms is decreased by two units. *If the two atoms are substantially alike in size and structure,* we may assume that this decrease in charge is to be divided equally between the two atoms. Thus if an atom in a compound has s electrons in its sheath and it has a covalence v_c then the effective charge of its sheath is $s - v_c$. The total charge of the atom may thus be taken as

$$e - (s - v_c) = v_e + v_c = v.$$

Thus v, the sum of the electrovalence and the covalence, for any atom in a compound, is equal to the *residual atomic charge.*

When two atoms which hold a duplet in common differ considerably in size, it is no longer obvious that the two electrons of the duplet should be divided equally between the two atoms in determining the residual charge. We may, however, arbitrarily so define the boundaries of the individual atoms in molecules that a duplet binding two atoms together is to be regarded as belonging equally to the two atoms. In this case we may consider v to be the residual atomic charge even when the atoms differ greatly in size.

It is evident from Coulomb's law that the separation of positive from negative charges requires in general the expenditure of work. The most stable forms of matter should be those in which the positive and negative charges are as near together as possible. However, we can not rely entirely upon Coulomb's law for this would indicate that the distance between unlike particles should decrease without limit. The exact distribution of charged particles in their most stable arrangement thus requires a knowledge of the repulsive forces whose existence we have already assumed. A further discussion of this point will be reserved for a future paper. At present we may attempt to express this relation by the following postulate.

Postulate 3.—The residual charge on each atom and on each group of atoms tends to a minimum.

By "residual charge" is meant the total charge of an atom or group of atoms regardless of sign. By "group of atoms" is meant any aggregate of atoms which are characterized by proximity to one another. It is felt by the writer that this postulate is a crude expression of a very important and fundamental law. When we understand the repulsive forces between charged particles better we shall be able to state the law in a more nearly quantitative form. The law is of very wide application. The uniformity of distribution of positive and negative ions in a salt solution is a familiar example of the working of this law. In any small finite element of volume the charges of the positive and negative ions tend to be very nearly equal or the residual charge tends to a minimum.

Postulate 3 expresses merely a strong *tendency* so that in general the charges of individual atoms are not necessarily zero. When the atomic charges depart from zero, however, they do so only as the result of a definite force or action which opposes the tendency of Postulate 3. We shall see that Postulates 1 and 3 are often in conflict and in such cases the tendency of Postulate 1 may prevail against that of Postulate 3.

We may now classify chemical compounds according to the types of valence exhibited by their atoms and will consider the application of Postulate 3 to each class of compound. There are 3 general subdivisions to consider:

(1) Complete Compounds, (2) Incomplete Compounds, and (3) Exceptional Cases.

1. COMPLETE COMPOUNDS. —All electrons are in complete layers of 2, 8, 18 and 32 electrons, in accordance with Postulate 1. Since Σv_c in Equation 4 can never be negative, Σv_e must always be either zero or negative. Therefore atoms having negative valences must always be present in a complete compound. Thus electropositive elements do not form complete compounds with each other.

a. Compounds Without Covalence.—$\Sigma v_c = 0$. Equation 4 becomes $\Sigma v_e = 0$, so that the sum of the negative valences in the compound must be the same as the sum of the positive valences. Since the residual charge v for each atom must equal $v_e + v_c$ it is evident that compounds without covalence must consist of positively and negatively charged ions. The charge v on each ion of complete compouds of this type is uniquely determined by the values of e for the elements forming the ion. This is a case where Postulates 1 and 3 are in conflict. The tendency of Postulate 3 by itself would make each atom electrically neutral, but this would leave the sheaths of the atoms incomplete and so fail to satisfy the tendency of Postulate 1. The result is a kind of compromise by which Postulate 1 may be satisfied by the formation of complete compounds *provided this can take place without the charges on the ions becoming too large.*

Although Postulate 3 does not definitely fix the charges of the individual atoms in the compounds we are considering, yet it does determine the distribution of these ions in space. This is a factor of prime importance in the crystal structure, in the electrolytic conductivity of substances when in the liquid state, and in other properties. It is also the cause of an interesting effect observed when the number of ions of one sign is much greater than that of the other sign, as for example in such compounds as $AlCl_3$, PCl_5, SF_6, etc. Postulate 3 requires that the negative halogen atoms in these compounds shall surround the most strongly positive atoms. The ions thus form groups having strong internal and weak external fields of force so that these constitute molecules of considerable stability and inertness towards outside influences. The volatility of these substances and the absence of electrolytic conductivity are due to this cause.

Typical examples of complete compounds without covalence are:

Salts.—When the atomic charges are small as in NaCl, $BaBr_2$, K_2S, etc., the salts are fairly readily fusible, soluble in liquids of high dielectric constant, good electrolytic conductors when molten or in solution and very difficultly volatile. With larger charges as in MgO, BN, Al_2O_3, etc., the strong forces give great infusibility, insolubility, hardness, etc., to the substance. Such compounds are exceptionally good electric insulators at moderate temperatures but are electrolytic conductors when molten.

Silicates, glasses, slags, complex sulfides, and most minerals, etc., are compounds which usually contain several electropositive elements. In the molten, and often in the solid condition, they are electrolytic conductors and are usually soluble in one another. The valence relation $\Sigma v_e = 0$ gives us no information in regard to the structure; for example, we can not write structural formulas for such compounds. The definite composition of many solid minerals, etc., is largely due to the regularities of the space lattices of their crystals.

Volatile halogen compounds such as AlF_3, PCl_5, SF_6 and structurally related complex ions such as SiF_6^{--} in the compound K_2SiF_6. Such high electrovalences as $+5$ for phosphorus, and $+6$ for sulfur can occur only when the tendency of Postulate 3 is counteracted by a particularly strong opposing tendency. In the case cited above it is the exceptionally great affinity of the halogen atoms for electrons that causes the action. The halogen atoms have this property in marked degree because they have larger charges on their kernels than other atoms and therefore exert a greater attraction on electrons (Coulomb's law). The fluorine atom has a greater affinity for electrons than the other halogen atoms since the radius of the atom is less and the force (by Coulomb's law) acting on the electron is greater.

b. Compounds Without Electropositive Atoms.—In these compounds the electrovalence of *every atom* must be negative, for if the electrovalence of any element is zero (inert gases) it can form no compounds. If we let v_n represent the numerical value of the negative valence we obtain from Equation 4

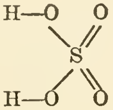
$$\Sigma v_c = \Sigma v_n. \qquad (6)$$

Since $v_n = s - e$, the value of v_n is fixed for any particular atom. For any given group of atoms, we can find Σv_c from (6) but we can not find the values of v_c for the individual atoms, in this way.

If, however, we place $v_c = v_n$ for each atom it is evident that Equation 6 will be satisfied. The residual charge on every atom (being $-v_n + v_c$) is then zero. Thus in any group of atoms *Postulates 1 and 3 are both completely satisfied if the covalence of each atom is equal to the negative valence of that atom.* The negative valence of carbon, nitrogen, oxygen and sulfur are 4, 3, 2 and 2 respectively, while that of hydrogen and the halogens is one. If therefore we follow the custom of the organic chemist and write structural formulas using these valences we obtain results in complete accord with Postulates 1, 2 and 3.

Thus these 3 postulates lead us to a rational derivation of the empirical valence rules which constitute the foundation of the science of organic chemistry. Moreover we are brought to see clearly the limitations of this empirical theory. We now realize that it is only *negative* valences that should be used in structural formulas (*i.e.,* as covalences) and that even these can only legitimately be used in compounds in which electropositive atoms are entirely absent, for if some of the atoms have a positive residual charge ($v = v_e$) then from Eq. 5 it is evident that other atoms must have a negative charge, and for these as well as the electropositive atoms the covalence is not equal to the negative valence.

From this viewpoint it is incorrect to write structural formulas such as Na – Cl,



etc., in which the covalence of one atom is taken as equal to the positive valence of that atom.

It should be kept in mind that Postulate 3 does *not require* that v_c should be equal to v_n. There is merely a tendency for these valences to be equal. Among compounds of electropositive elements we saw that there was a conflict between the tendencies of Postulates 1 and 3 so that v was always different from zero. With compounds formed exclusively of electronegative atoms, however, there is not necessarily a conflict and it is for this reason that we have such a large class of compounds in which v is zero (*i.e.,* $v_c = v_n$). There may be various causes that make it difficult for v to be zero even for some compounds of electronegative elements, so that in individual cases v may differ from zero by one or two units. It must be remembered that we deduced the relation $v =$ *minimum* from Postulate 3 only by assuming the two atoms which share a duplet are of substantially the same size, etc. From Coulomb's law we should expect that either a large charge on the kernel of an atom or a small radius for the kernel should cause electrons in the sheath to be held more firmly and should make it easier for the atom to acquire a negative residual charge. As an example let us consider the electronegative elements of the first two periods.

As we pass from carbon, through nitrogen and oxygen, to fluorine, the kernel charge increases and the size of the kernel presumably decreases. The residual atomic charge should thus tend to become more negative as we pass towards fluorine and more positive in comparison as we pass towards carbon. In other words in compounds of these elements, we should expect a tendency for fluorine to have a covalence a little less than its negative valence while for nitrogen the covalence should tend to be greater than the negative valence. Since there are only eight electrons in the sheath of these atoms, the covalence of the carbon atom can never exceed four. All these conclusions are in perfect accord with experience. Thus we find the following covalences:[4]

Carbon	*4*	(3)			
Nitrogen	4	*3*	(2)		
Oxygen		(3)	*2*	1	0
Fluorine				1	*0*
Silicon	4 (or electro-positive)				
Phosphorus	*4*	3			
Sulfur	4	3	2	1	0
Chlorine	(4)	(3)	(2)	*1*	*0*

In this table the numbers in italics give the most common valences, while those in parentheses are only rarely found. It is clear that a large kernel charge favors covalences less than the negative valences while a small kernel charge has the opposite effect. A comparison of the elements of the second period with those of the first, shows a slight tendency for larger covalences among the heavier elements. This is to be explained as the effect of the larger kernel and hence weaker forces. There is also much more scattering among the valences of the heavier elements. This is another result of the weaker forces acting on the electrons for the covalence of such atoms is more dependent upon the electron affinity of the other atoms with which they are combined.

As an example of these relationships, let us consider the compounds, CH_4, NH_3, H_2O, and HF. In each atom of these compounds the covalence is equal to the negative valence so that the residual charge is zero and the tendencies of Postulates 1 and 3 are satisfied. If we mix the NH_3 and HF together the larger kernel charge of the fluorine as compared with the nitrogen, gives a tendency for the fluorine atom to become negative at the expense of the nitrogen. Thus the covalence of the fluorine decreases to zero while that of the nitrogen increases to four. This leads to the formation of the compound NH_4F which consists of NH_4^+ ions and F^- ions. The total number of covalence bonds has not been changed, they have merely been distributed differently. But this causes the atoms to become charged and makes the compound an electrolyte. It should be noted that this theory indicates definitely in what direction the change of charge occurs. Thus we should not expect NH_3 and HF to give a compound consisting of ions NH_2^- and H_2F^+ although under other conditions these ions might exist.

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[4] See I. Langmuir, *Jour. Amer. Chem. Soc., 41,* 927 (1919).

Similarly NH_3 and H_2O may react to form NH_4OH which will consist of ions NH_4^+ and OH^-. But the tendency to form a compound such as this is much less than in the case we have just considered, for the charge on the kernel of the oxygen atom is less than that of the fluorine atom so it has less tendency to become negative. As a result NH_3 is much less active towards H_2O than towards HF. Examples of this kind can be extended almost indefinitely and can even be used to obtain quantitative relationships between the heats of formation of various substances.

Since the sheaths of atoms of atomic number less than about 25 never contain more than 8 electrons, the covalence of these atoms can not exceed 4. With heavier atoms, however, we might expect in some cases larger covalences than 4. Large covalences are improbable in most cases for they imply equally large negative valences which means that the number of electrons in the sheath must be very much larger than the charge of the kernel. There are a few compounds, however, which suggest that large covalences sometimes exist. For example the compounds $Fe(CO)_5$ and $Ni\ (CO)_4$ correspond to complete compounds in which the central atoms have the covalences 10 and 8 respectively. Since e for iron is 8 and for nickel is 10 and the complete sheaths for these atoms contain 18 electrons, the negative valences of iron and nickel are 10 and 8, that is the same as the covalences needed to account for the above compounds. Thus these compounds are in accord with both Postulates 1 and 3, and are to be regarded as of a type analogous to organic compounds in which the covalence of *every atom* is equal to its negative valence. It should be noted that both of these compounds are liquids of low boiling point (102° and 43°) and their molecular weights have been determined. Their properties are about those to be expected if they have the structure assumed above. Other compounds of iron with carbon monoxide are known, but they have only been obtained in the crystalline state and their molecular weights are unknown.

Molybdenum carbonyl, $Mo\ (CO)_6$,[5] is a very easily *volatile* crystalline compound. It is interesting to note that the *negative valence* of molybdenum ($s - e = 18 - 6$) is twelve, so that with a covalence of 12 for the molybdenum atom in this compound we again obtain a structure consistent with the valence theory discussed above.

[5] Mond, Hirtz, Cowap, *J. Chem. Soc.*, *97*, 798 (1910).

2. Incomplete Compounds.—These are compounds in which some of the electrons are not arranged in complete layers or sheaths, so that the tendency of Postulate 1 is not completely satisfied. This can only occur as a result of a conflict between Postulate 1 and Coulomb's law or Postulate 3. We have seen that the tendency of Postulate 3 causes the residual charge (v) on each atom to be a minimum. The tendency of Postulate 1, however, is sufficiently strong to force the atoms to take up charges of 3, 4, or even under some conditions, 5 or 6 units, if this should be necessary in order to bring all the electrons into complete layers. Since there must be a limit to the strength of the tendency of Postulate 1 it is not surprising that residual atomic charges greater than 4 or 6 are very rare. Now the atoms of the elements near the middles of the long periods (of 18 and 32 elements), do not become complete even if they do acquire residual charges as great as 5 or 6 units, and it is therefore natural that the tendency of Postulate 3, which must become stronger as the charge increases, should prevent the formation of complete compounds of these elements. There are two types of incomplete compounds to consider.

a. Metallic Substances. Electronegative Atoms Absent.—By Coulomb's law, atoms having only small charges on their kernels, should not be able to take up enough electrons to complete sheaths of 8 or more electrons. Thus if we bring together a number of electropositive atoms there is no way in which the electrons in the incomplete sheaths can rearrange themselves to form complete sheaths. The "free" electrons which are thus compelled to remain in incomplete sheaths are responsible for the metallic properties shown by all electropositive elements in the solid or liquid state. It is clear, however, notwithstanding the fact that hydrogen may sometimes function as an electropositive element, that liquid or solid hydrogen should have none of these metallic properties according to this theory, for the sheath to be formed in this case contains only two electrons. The forces acting between the free electrons and the kernels of the atoms in metallic substances, are of the same order of magnitude as in salts, so that metals have about the same range of vapor pressures, hardness, compressibilities, etc., that are shown by salts.

In general, all atoms must be electropositive unless they can take up enough electrons to complete their sheaths and thus act as electronegative atoms. The tendency of Postulate 3 ordinarily prevents the occurrence of negative valences greater than about 4. In the two short periods eight electrons are needed to form a complete sheath so that the elements with kernel charges greater than about 3 can act as electronegative atoms and therefore do not normally show metallic properties. In the 2 long periods 18 electrons form the complete sheath so that about the first 14 of the elements in each of these periods can usually act only as electropositive elements and they thus have metallic properties, when in the elementary form. For similar reasons all the known elements of the rare earth period (the last two being unknown) have metallic properties.

b. Compounds Containing Electropositive and Electronegative Atoms.—As a result of Coulomb's law or Postulate 3, the positive valence of an element is usually limited to a value of 2 or 3 unless particularly strong forces are exerted to draw away electrons, and thus raise the positive valence a few units higher. Thus in the middle of the long periods the charges of the kernels are so great that all the electrons in the sheaths of the electropositive atoms can not be given up even when other atoms are present that can take up electrons. It thus happens that the long periods contain series of elements which all have 3 or 2 and 3 as their principal valences. The atoms of these elements are therefore incomplete. The electronegative atoms in such compounds, however, are always complete.

It is of interest to note that as long as atoms are incomplete there seems to be no tendency for them to have an even rather than an odd number of electrons. For example, the following ions all have odd numbers of electrons: Cr^{+++}, Mn^{++}, Fe^{+++}, Co^{++}, and Cu^{++}. This seems to indicate that the remarkable tendency, pointed out by Lewis, for most compounds to contain even numbers of electrons is due merely to the relative abundance of complete compounds as compared to incomplete ones. In other words, the even number of electrons in most compounds results from the tendency of Postulate 1 rather than from any more general tendency for electrons to form pairs.

Many of the compounds of this class, such as ZnO (zincite), Fe_3O_4, PbS, CuO, etc., show electric conductivity even as solids. This is undoubtedly caused by the relatively large number of electrons in incomplete sheaths. Of course we should not expect all compounds which contain such electrons to show conductivity, for the presence of the electronegative atoms might easily prevent the mobility of these electrons. We need to know much more than we now do about the arrangement of the atoms and their electrons in space before we can predict conductivity in particular cases of this kind.

3. Exceptional Cases.—There are some substances or compounds whose structure is not adequately accounted for by the foregoing analysis. A few examples are: N_2, CO, CN^-, NO. The writer believes these have the single octet structure which he described in his earlier publications. It is probable that acetylene, C_2H_2, and the carbide ion C_2^{--} (in CaC_2, etc.) have the same kind of structure. Pease has suggested that they may all have a triple bond structure.[6] This question merits careful study.

[6] *Jour. Amer. Chem. Soc., 43,* 991 (1921).

Another set of compounds that must have a special structure are various compounds of boron such as B_2H_6.

Most compounds containing molecules of H_2O, NH_3, etc., are readily accounted for by Postulate 3 but many of these should be considered by methods somewhat different from those developed here.

In double molecules such as H_4O_2 (in ice), H_2F_2, and in compounds such as KHF_2, etc., it seems that the hydrogen nuclei instead of forming duplets with electrons in the same atom, form duplets in which the two electrons are in different atoms. The hydrogen nucleus itself thus acts as a bond in such a case. Latimer and Rodebush have made a somewhat similar suggestion in regard to hydrogen nuclei acting as bonds. They consider, however, that the hydrogen nucleus acts on two pairs of electrons: one pair in each of the two atoms. It seems to the writer much more probable that the hydrogen nucleus is no more able to attract four electrons than is the nucleus of other atoms. Since the first layer of electrons in all atoms contains only 2 electrons it seems probable that the hydrogen in this case also holds only two electrons and that these form the definite stable group which we have termed the duplet.

The writer plans to consider the quantitative aspects of these valence theories in subsequent papers. It is aimed to put Postulates 1 and 3 into a form that will permit at least rough calculations of the relative stabilities of various substances as measured, for example, by their heats of formation.

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*Ind*ustrial and *Eng*ineering *Chem*istry.
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*Gen*eral *E*lectric *Rev*iew.
*Proc*eedings of the *Amer*ican *Phil*osophical *Soc*iety.
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